Part 1. An absolute method tor the measurement of reflectivity. Part 2. The distribution of heavy metals in granites

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Part 1. AN ABSOLUTE METHOD FOR THE MEASUREMENT OF REFLECTIVITY

Part 2. THE DISTRIBUTION OF HEAVY METALS IN GRANITES

A thesis submitted for the Degree of
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Abstract

Part 1. An Absolute Method for the Measurement of Reflectivity

Because of the difficulty in establishing reflectivity standards for use in the measurement of reflectivity by comparison, the present method was developed to allow the measurement of absolute reflectivity at perfectly normal incidence. A glass cube with a semi-metallised surface was mounted in the centre of a horizontal circle goniometer, a photomultiplier clamped over the viewing telescope and the specimen supported in front of the glass cube. Monochromatic plane polarised light was passed through a system of lenses which cause the now parallel light beam, after passing through the cube, to fall on the specimen surface with perfectly normal incidence. Facility is provided for measurements in both air and oil. A mathematical treatment of the intensity relationships of the various direct and reflected light rays is given, from which the reflectivity of the specimen (and also the glass cube) can be calculated. The reflectivity of several standard samples in both air and oil is recorded.

Part 2. The Distribution of Heavy Metals in Granites

The present survey was conducted in order to extend the possible application of primary cycle geochemical prospecting. Nine different areas of Hercynian and Caledonian granites in Great Britain were studied and both trace and major element analyses recorded. Care was taken to include only unweathered samples for analyses, and three mineral fractions, namely, biotite, muscovite and feldspar plus quartz were separated and analysed independently. A method for calculating the plagioclase, orthoclase and quartz percentages in the feldspar plus quartz fraction by the use of x-ray diffraction is given. Analyses are included to show the variation of trace elements away from a mineral vein, the variation of element concentration within a given granite, and the number of samples required to detect a significant difference between two trace element populations. As well as discussing geochemical prospecting, details of the degree of fractionation and order of intrusion of different phases of the same granite, and comparisons between different granites, are given.

PART 1

AN ABSOLUTE METHOD FOR THE MEASUREMENT OF REFLECTIVITY

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INTRODUCTION

One of the first recorded instances of the use of reflectivity for the identification of opaque minerals is by Inostranzeff (1885), who made a simple visual comparison between samples with prepared surfaces. Since that date, the apparatus for the routine determination of reflectivity has become far more sophisticated and much more accurate, but the method is still basically one of comparison. The available absolute methods for determining reflectivity are limited in number and suffer from two disadvantages; firstly, the reflectivity is determined, not at truly normal incidence but rather at angles up to ten degrees, and secondly, it is not usually possible to determine the reflectivity of the specimen in an immersion medium other than air. The technique developed here overcomes these two disadvantages and makes possible absolute measurements of reflectivity at perfectly normal incidence, in both air and oil.

Theory of Reflected Light

Reflectivity

For an isotropic transparent body, the reflectivity, R, at normal incidence (the ratio of the reflected light intensity to the incident intensity) depends on the refractive index of the specimen, n, and of the medium, N, which covers the specimen. The relationship is represented by the equation:-

$$R = \frac{(n - N)^2}{(n + N)^2} \qquad (1)$$

In vacuum, and to a close approximation in air, N is equal to one. This equation and the ones to follow were derived originally by Fresnel (1866 - 70) and more recently have been discussed by such authors as Cambon (1949), Cameron (1961) etc.

For an opaque body, an appreciable amount of light energy is absorbed and the absorption index, K, must be included in equation (1), which becomes:-

$$R = \frac{(n - N)^2 + n^2K^2}{(n + N)^2 + n^2K^2} \qquad (2)$$

Anisotropic opaque minerals have different refractive indices and absorption indices in the different optical directions. This means that the reflectivity also changes with direction, (and experience has shown) that for an anisotropic section of such a mineral there are two principal directions at right angles, such that at normal incidence, for vibrations parallel to the two directions, the reflecting powers are:-

$$R_1 = \frac{(n_1 - N)^2 + n_1^2K_1^2}{(n_1 + N)^2 + n_1^2K_1^2} \qquad (3)$$

$$R_2 = \frac{(n_2 - N)^2 + n_2^2K_2^2}{(n_2 + N)^2 + n_2^2K_2^2} \qquad (4)$$

By convention R_1 is greater than R_2. If THE PLANE OF POLARIZATION OF the incident light beam makes an angle α with R_1 the equation becomes:-

$$R = R_1\cos^2\alpha - R_2\sin^2\alpha$$

Rotation on reflection due to anisotropy

The inequality of reflectivities causes a rotation of the reflected vibration. Orcel (1925) has shown, that with a section of principal reflectivities R_1 and R_2, if the vibration direction of the incident polarised light makes an angle r with the direction R_2, the polarised beam is turned through an angle w on reflection, given by:-

$$\tan w = \frac{(\sqrt{R_1} - \sqrt{R_2})\sin r \ .\cos r}{\sqrt{R_2}\cos^2 r - \sqrt{R_1}\sin^2 r} \qquad (5)$$

From this equation it is seen that the reflection approaches the direction of vibration of the privileged direction associated with the greater of the principal reflectivities of the section. As the anisotropy of reflection R_1/R_2, has values close to unity, the angle is a maximum near $r = 45^\circ$.

Reflection at Inclined Incidence

Cambon, (1949), reports that for angles near normal incidence reflectivity varies very little with the angle of incidence, so that reflectivities measured at low magnification with the microscope, i.e., with slightly converging light, are the same, to a first approximation, as the reflectivities measured at perfectly normal incidence. Berek, (1955), showed experimentally that the smallest difference between two reflectivity readings of the same sample taken with a 0.1 and 0.3 numerical aperture objective respectively, was 1.25%, and errors as large as 3% were found. Berek also reports differences of up to 20% for reflectivities from 0.1 and 0.9 numerical aperture objectives. Furthermore, for anisotropic minerals, the values desired are R_1 and R_2. These can be measured, in perpendicularly incident light, simply by measuring the reflectivity first at one extinction position and then at a second 90° from the first. Under the microscope however, owing to the effect of convergence, measured values of R_1 and R_2 will vary with the aperture of the objective. Cameron, (1961), states that for the present there is no means of determining these values for anisotropic minerals that can be reproduced from laboratory to laboratory, and only the mean reflectivities will be reproducible. However, Cameron does say that the measured values for R_1 and R_2 will always be the same for any one apparatus and after calibration it can be used for experimental purposes.

Rotation of the reflected beam due to divergence between the plane of polarisation and the plane of incidence

It can be easily shown that if, 1. the angle of incidence of the incident light beam is 0° or 90°, or 2. the plane of vibration of the polarised light beam is parallel or perpendicular to the plane of incidence (the plane defined by the incident and reflected rays and the normal to the surface) there will be no rotation of the reflected or refracted beam. A more rigorous treatment of this matter is given in several text books, e.g. Cameron, (1961).

Variation of reflectivity with wavelength

It has been known for some time that the refractive index, and therefore the reflectivity, varies with the wavelength. It is common practice therefore, to quote reflectivities at different wavelengths. Not only does this avoid the error due to the different colour temperatures of the different lamps, and minimise the effect of the different spectral response of different light intensity detectors, but also the variation of reflectivity with wavelength may prove helpful in identifying the specimen if sufficiently accurate measurements are made.

Previous Work

Measurement of reflectivity

The first real attempts to measure reflectivity were all made using a photometer; this is a device, whereby the image of the mineral surface is brought into juxtaposition in the ocular with a field of light whose intensity is calibrated and can be varied. The intensity of the calibrated variable field is adjusted so that it is equal to that of the image of the mineral. If determinations are made on known and unknown specimens a comparison is possible. Such measurements were first made by Schneiderhohn, who made his observations using a slit microphotometer, made especially for him by M. Berek. Schneiderhohn did most of his work using this apparatus between 1922 and 1930 and much of his data appears in Schneiderhohn and Ramdohr (1934), and Schneiderhohn (1952). An excellent description of the Berek slit microphotometer is given in English by Short (1940). Schneiderhohn and Ramdohr (1934), described a photo-electric photometer based on the use of a barrier layer cell, and in 1937, Malmquist described a photometer incorporating two barrier layer cells arranged in opposition to one another. More recently, Hallimond (1957), described a photometer which used three polarising screens to provide a primary scale for measuring the ratio of the intensity between the incident and reflected beam.

Also developed for measuring reflectivity, but starting at a slightly later date, were photo-electric cells. These cells convert light energy into electricity, and so a direct measure of the reflected light intensity can be made.

Orcel (1927 and 1930), was the first person to apply the photo-electric cell to reflected light work. This was closely followed by Schneiderhohn and Ramdohr (1934), and Moses (1936), all working independently; and slightly later by Cambon (1949), who used much the same technique as Orcel. Working at the same time as Cambon, Folinsbee (1949), described the simple, but not too accurate, measurement of reflectivity by the use of a photographic exposure meter. More recently, Bowie and Taylor (1958), described the use of a photo-electric device; Cameron (1961), also used photo-electric means for measuring reflectivity; and Evans Electroselenium Limited have incorporated a barrier layer photocell and an optically amplified reflection galvanometer into a commercially available unit. Jones (1962), concerned especially with the very low reflectivity of coal, combined a photomultiplier with a Berek photometer. By placing in the light beam a polariser which rotated at three thousand revolutions per minute, Jones produced a sine-wave modulation which he was able to amplify and thus measure, by means of the amplified beam, very low reflectivities.

To compare the photometric and photo-electric means of measuring reflectivity, Murchison (1960), conducted a series of experiments with a Berek photometer, and concluded that the subjective factor was small, and that the accuracy was as great as with a photo-electric cell. Shaw and Chandra (1953), and Wege (1954), both working specifically on coal, compared results taken on the same specimen by both methods, and because the results did not differ significantly, they concluded that both methods were comparable.

Photo-electric devices however, have three draw-backs which photometric devices do not have. First of all, small variations in the polished surface can affect the reflectivity; using a photometric device only a small area of the field of view need be used, and even then scratches and blemishes can be allowed for subjectively. Secondly, small fluctuations in the incident light intensity will cause great instability with photo-electric devices, but seem to make little difference to photometric techniques. Thirdly, the polished section must be exactly level or errors will result; experiments by Moses (1936), showed that if the specimen was off horizontal, by as little as one or two degrees, a one per cent error could arise.

However, the greater range, in particular for lower reflectivities, plus the elimination of the subjectivity factor, and greater speed of measurement all seem to have made the photo-electric cell more popular than photometric devices.

Measurement of the refractive index and the absorption constant

If two measurements of reflectivity are made, one, Ra, in air, and the other Ro, in oil, it can be seen that after substituting these two values successively into equation two, there are two equations in two unknowns. From these two equations we get a solution for the refractive index and absorption constant:-

$$n = \frac{(N^2 - 1)/2}{N\frac{(1 + Ro)}{(1 - Ro)} - \frac{1 + Ra}{1 - Ra}}$$

$$K^2 = \frac{Ra(n + 1)^2 - (n - 1)^2}{n^2(1 - Ra)}$$

Several workers in the past have taken measurements in both oil and air and so calculated the absorption constant and the refractive index, e.g. Cambon (1949), Kaemmel (1962), and Nichol (1962). All workers reported difficulty in obtaining reliable results for the reflectivity in oil.

Reflectivity standards

As already stated, both the photo-electric and photometric routine methods of determining reflectivity are only relative, in that they require some standard with which the unknown sample can be compared. This standard should be; - firstly, reproducible so that different workers can compare results. Secondly, durable, i.e. maintain its identical reflectivity for some time and not tarnish. And, thirdly, fall into approximately the same reflectivity range as the specimen to avoid errors due to non-linearity of the apparatus. For the third reason it would be desirable to have three or four standards covering the whole range.

Berek (1953) recommended for the calibration of his microphotometer a basal plate of quartz three to four centimetres thick. Although the reflectivity of quartz can be calculated by experimentally measuring its refractive index, its reflectivity, about 5%, is well below the average for ore minerals. Cissarz (1932), included sphalerite and galena as reflectivity standards; unfortunately the iron content in sphalerite can rise as high as 26%, causing the reflectivity to vary by as much as 7%. Although galena, and also pyrite which was regarded for some time as the best reflectivity standard, are easily obtained, Santokh Sing (1965) has shown that pyrite from different localities has different reflectivities so that it is not an ideal standard. Several workers have also found that reflectivity varies with polish, e.g. Berek (1953), found that the reflectivity of a cleaved surface of stibnite dropped by 4.3% after careful polishing, by 12.4% after severe polishing and by 18.1% after dry polishing. Cissarz, (1932), also compared polished and cleaved surfaces and found a drop in reflectivity of 1.5%, 1.8% and 3.6% for sphalerite, galena and stibnite respectively. Specimens of diamond have also been used, and because diamond requires no polishing and does not tarnish it appears quite satisfactory. Its reflectivity however, is only 17% and again is too low for comparison with many ore minerals. Recently, some workers have reported a reproducible polishing method (Bowie and Henry (1964), and Cameron, (personal communication), and so this error can now be avoided.

Various attempts to obtain artificial standards, such as pure crystals of silicon and germanium (Cameron, personal communication) grown in the laboratory, and metals evaporated onto glass (e.g. Hallimond, 1957) have proved slightly more successful than natural minerals but are still not ideal. Cameron, (1961), p.110), summarised the problem when he said, "at the present time, there are no internationally accepted standard values for reflectivity".

Theory of this Absolute Method for Determining Reflectivity

To overcome the difficulties mentioned in the section titled "Oblique reflection" an apparatus was designed to give a light beam of perfectly parallel plane polarised light, in such a manner that it would strike the surface of the specimen at perfectly normal incidence. In order to measure the intensities of the incident and reflected light beams, a surface designed to reflect a reasonable proportion of the beam and transmit the remainder was placed in the path of the light beam as shown in diagram 1.

In Diagram 1 PP is a glass slip of reflectivity R (for oblique incidence) placed in a vertical plane at the centre of a horizontal circle optical goniometer, at 45 degrees to a plane polarised parallel light beam of intensity I_o. The vibration direction of the polariser should be either perpendicular or parallel to the surface of the glass slip so that no rotation of the plane of polarisation will occur on reflection. The surface QQ of the specimen whose reflectivity S is to be determined is set up at right angles to the light beam. This orientation and that of the glass slip is easily obtained by observation of the reflected beams with the telescope of the goniometer, in conjunction with the angular scale.

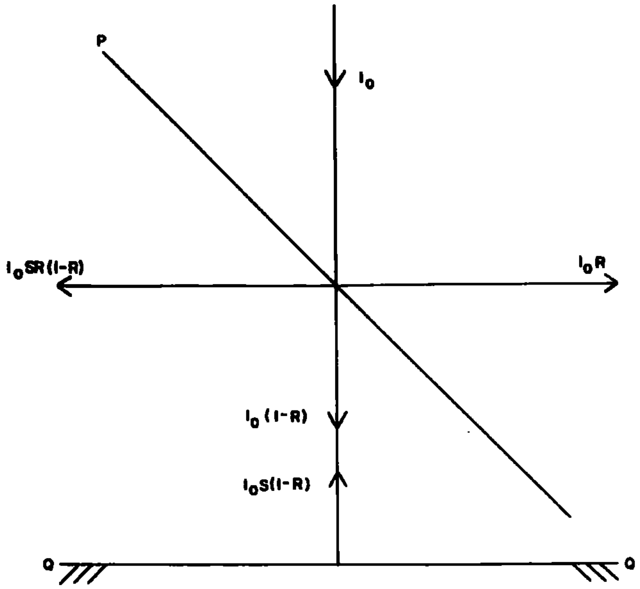


DIAGRAM 1 RAY DIAGRAM

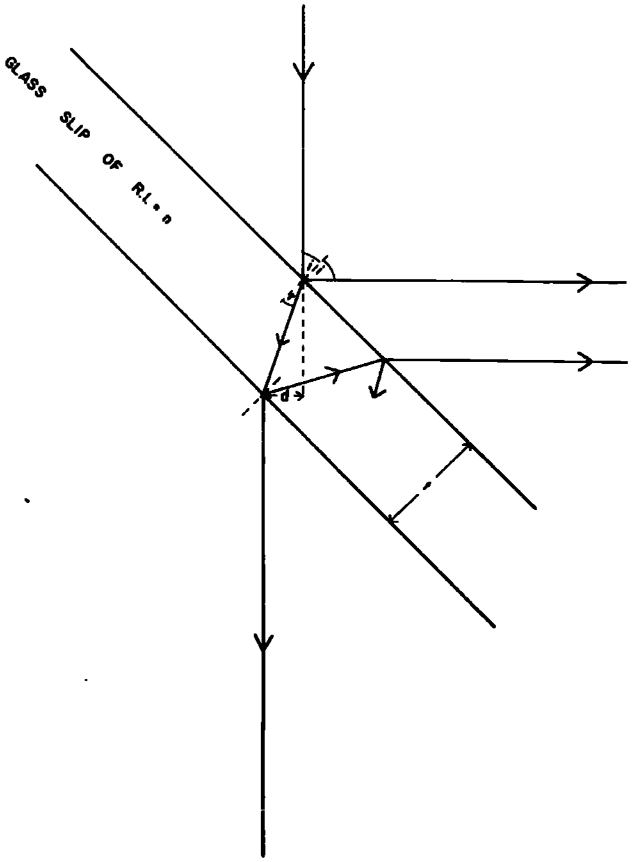


DIAGRAM 2 DISPLACEMENT OF A LIGHT BEAM AFTER PASSING THROUGH A GLASS SLIP

If a sensitive device for measuring light intensity is now attached to the telescope, the intensities $I_oSR(1 - R)$ and I_oR can be measured. The specimen and glass slip are then removed and the intensity I_o of the direct beam can be measured. R and S can then be calculated.

The simple relationship described above cannot be realised in practice because of internal reflections within the glass slip and because of displacement of the light beam as shown in diagram 2. The displacement of the light beam, d, is directly proportional to the thickness of the glass slip, t, the angle of incidence i, and the refractive index n. For most substances the refractive index is such that the displacement is not greater than ¼ of the thickness, and in any case, for an angle of incidence of 45° the displacement cannot exceed the thickness. By the use of a glass cube with a very thin reflecting diagonal, such as used in certain types of optical apparatus, the disadvantage of the displacement of the light beam is overcome. There will still be internal reflections between the faces of the cube, but because of normal incidence these can be allowed for in calculation. Also the diagonal of the cube has a much higher reflectivity than the simple glass slip, so reducing the problem of measurement.

From theoretical considerations (Conn and Bradshaw, 1951), it can be shown that when non-polarised light reflects from an inclined surface, it is resolved into two polarised beams at right angles. If the reflecting surface is held vertical but inclined at 45° to the incident light beam, then the reflection of a polarised light beam with vertical vibration, Rs, is:-

$$Rs = \frac{\sin^2(i-r)}{\sin^2(i\ r)}$$

and reflection of a polarised light beam with horizontal vibration, Rp, is:-

$$Rp = \frac{\tan^2(i-r)}{\tan^2(i\ r)}$$

where i is the angle of incidence and r the angle of refraction. If $i = 45^\circ$, for a glass slip of refractive index 1.50 it is found that $Rs = 0.093$ and $Rp = 0.0087$. It is advantageous in order to simplify the ray diagrams and mathematics to use polarised light, and because polarised light with vertical vibration gives the strongest reflection it was used.

As already shown, if the plane of polarisation is parallel or perpendicular to the plane of incidence there will be no rotation of the reflected or refracted beam. Also, because both halves of the glass block have exactly the same refractive index, the beam will have exactly the same direction on both sides of the semi-metallised diagonal; and because the diagonal is very thin, (see the description of the glass cube) there is negligible displacement of the rays. At the four boundary faces of the cube, the light beam is at perfectly normal incidence on the glass surface and so no rotation or refraction occurs. It can be seen therefore, that at ALL surfaces in the system no rotation of the plane of polarisation occurs, and, the angle of incidence is always equal to the angle of reflection. Although the increased number of rays due to successive reflections becomes very confusing, the basic principle is still the same. The successively reflected rays will be dealt with mathematically in the next section.

Diagram 3 shows the system without the specimen in place, when the viewing telescope is directly in line with the primary light beam. When the specimen is in place, and the telescope is at right angles to the primary light beam, the picture is almost exactly the same, except for one more reflection from the specimen, as shown by the plan view given in diagram 4.

With the proper use of the lamp condenser and iris, and the image collimator (see procedure), perfectly parallel light will leave the image lens, and be normally incident on the specimen surface.

Calculation of the intensity of the different light rays

The general method for calculating the intensity of the light rays was established by Dr. R.A. Smith (Durham University Mathematics Department) and the mathematics was completed in large part by Dr. Smith with assistance from Mr. R. Phillips and the author.

Diagram 5 shows the general case of a specimen whose reflectivity at normal incidence when immersed in oil is to be determined. I_x

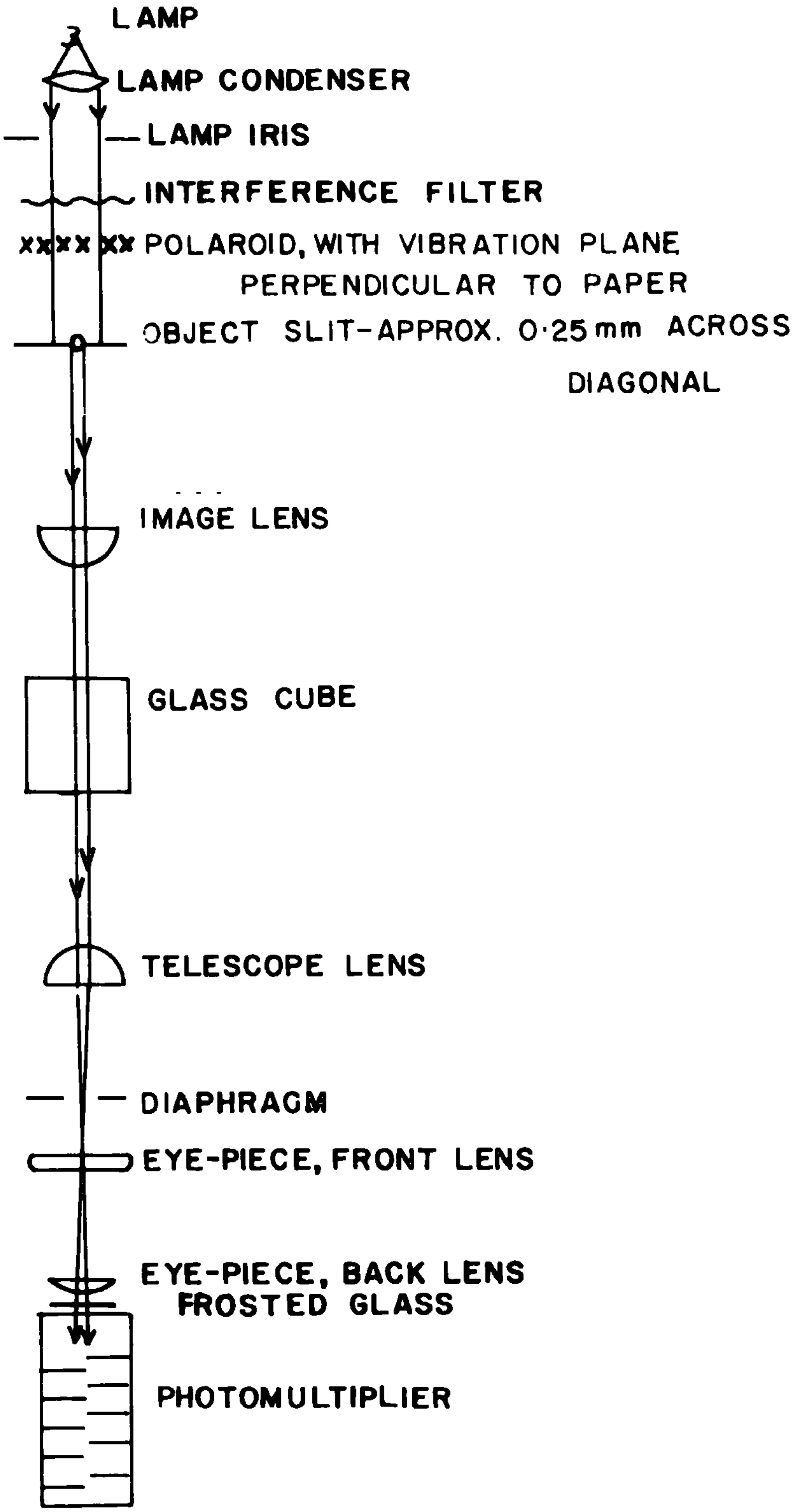
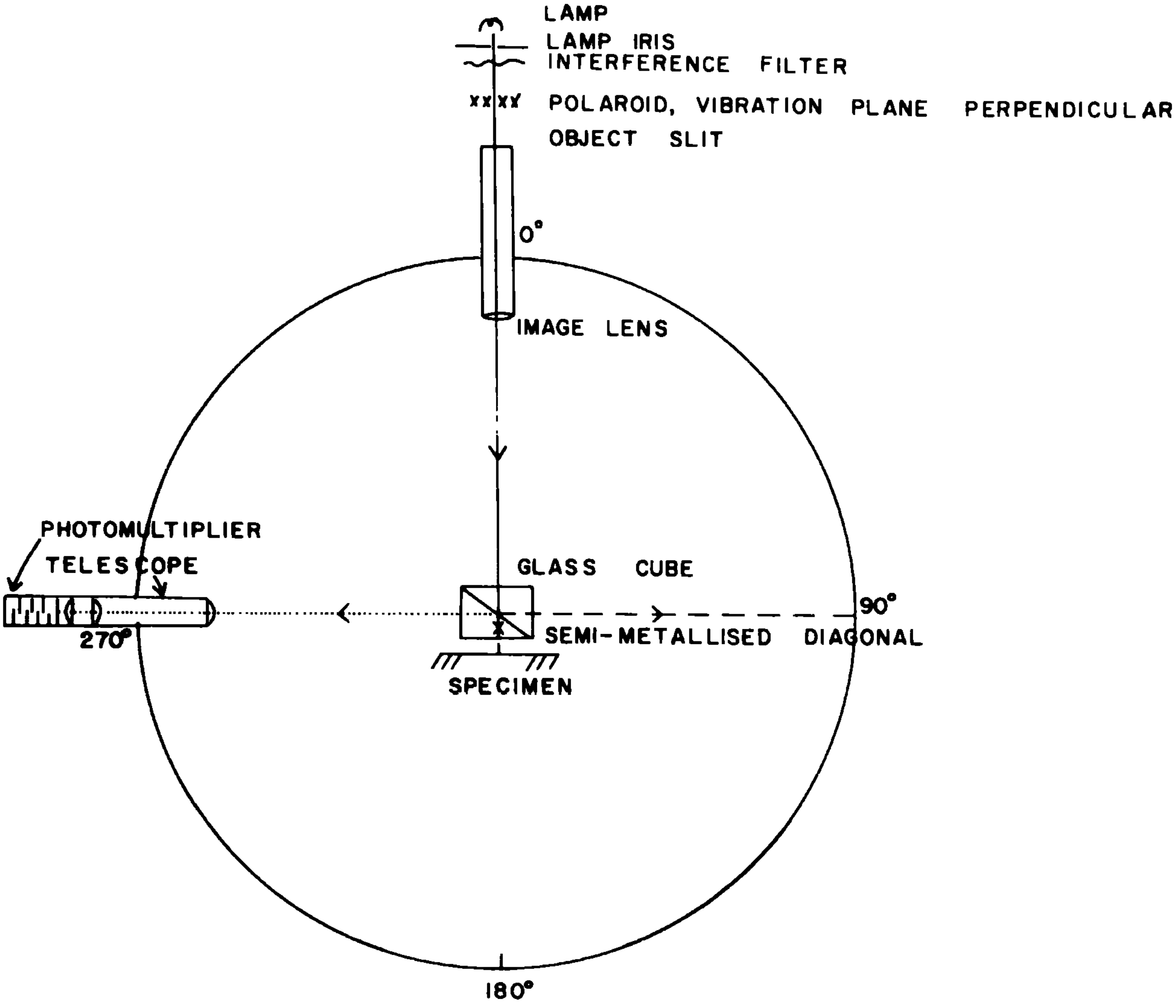


DIAGRAM 3 RAY DIAGRAM APPARATUS FROM CROSS-SECTIONAL VIEW



DIGRAM 4 PLAN VIEW WITH SPECIMEN IN PLACE

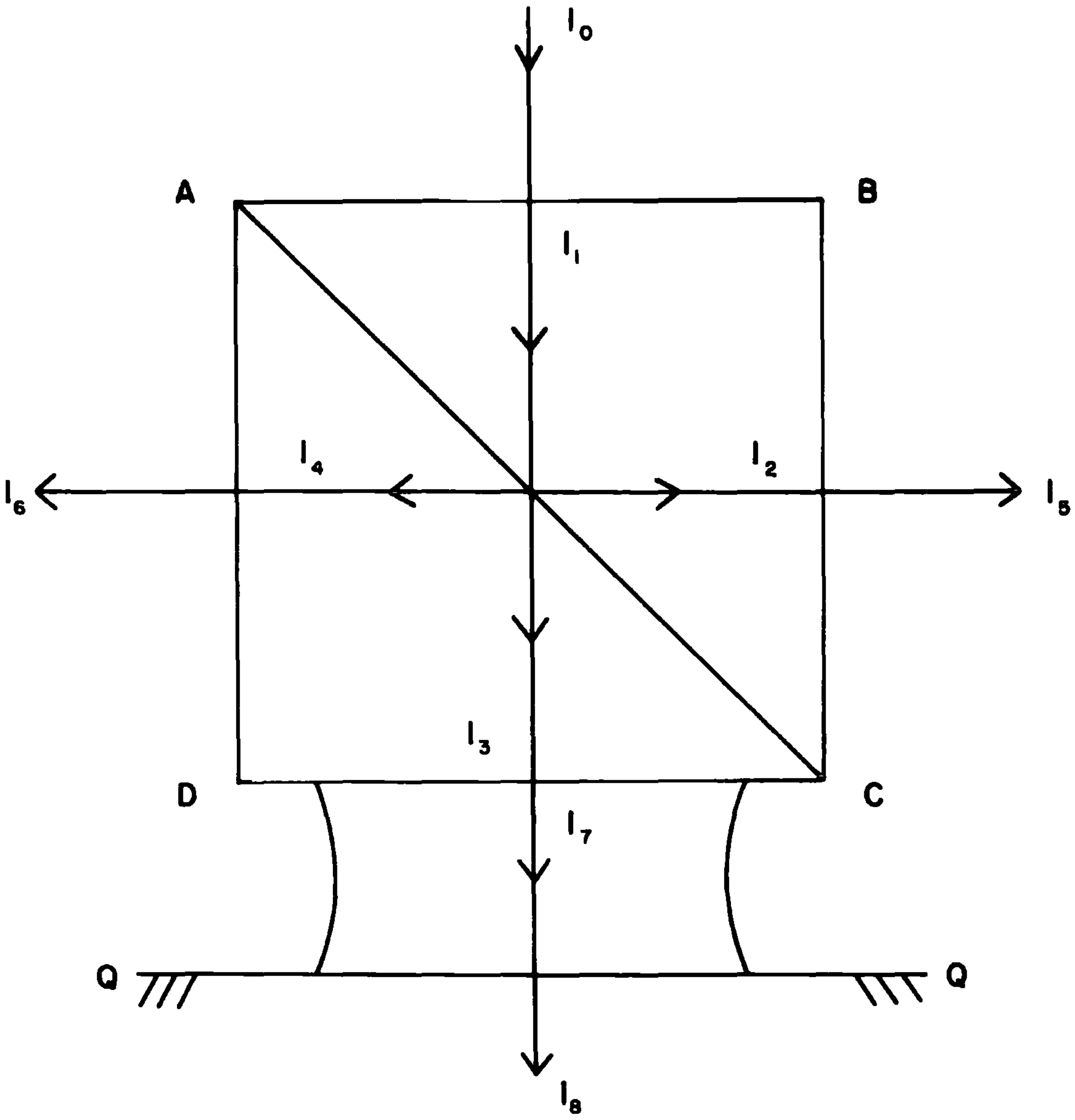


DIAGRAM 5 RAY DIAGRAM WITH SAMPLE IN OIL

denotes the intensity of light travelling in the direction shown by the arrow. J_x denotes the intensity of light travelling along the same path but in the opposite direction to I_x. Both I_x and J_x may involve several components, due to multiple reflections. The space between the face CD of the cube and the specimen surface QQ is filled with a liquid of refractive index n, (the thickness of the layer is greatly exaggerated in the diagram for clarity).

Let

r = reflection coefficient of the glass in air for normal incidence
w = reflection coefficient of the glass in refractive index n for normal incidence
S = reflection coefficient of the specimen in air for normal incidence
σ = reflection coefficient of the specimen in refractive index n for normal incidence
ρ = reflection coefficient of the diagonal for 45° incidence
θ = transmission coefficient of the diagonal for 45° incidence
$\rho + \theta \neq 1$ i.e. absorption in the diagonal cannot be neglected.

Of these quantities, w can be calculated from r knowing n, leaving five to be determined. For this purpose, the following quantities can be determined experimentally:-

$$\frac{I_5}{I_o}, \quad \frac{I_6}{I_o}, \quad \frac{I_5^1}{I_o}, \quad \frac{I_6^1}{I_o}, \quad \frac{I_7^1}{I_o}$$

where the prime indicates a reading with the sample PQ removed and J_7 consequently zero.

The following equations can now be derived:-

Equations for light leaving the

cube face AB
$$I_1 = rJ_1 + (1 - r)I_o \tag{1}$$
$$J_o = rI_o + (1 - r)J_1 \tag{2}$$
BC
$$J_2 = rI_2 + (1 - r)J_5 \tag{3}$$
$$I_5 = rJ_5 + (1 - r)J_2 \tag{4}$$
CD
$$J_3 = wI_3 + (1 - w)J_7 \tag{5}$$
$$I_7 = wJ_7 + (1 - w)I_3 \tag{6}$$
DA
$$J_4 = rI_4 + (1 - r)J_6 \tag{7}$$
$$I_6 = rJ_6 + (1 - r)I_4 \tag{8}$$

diagonal AC

$$I_2 = \rho I_1 + \theta J_4 \tag{9}$$
$$I_3 = \rho J_4 + \theta I_1 \tag{10}$$
$$I_4 = \rho J_3 + \theta J_2 \tag{11}$$
$$J_1 = \rho J_2 + \theta J_3 \tag{12}$$

Assuming no internal reflection from the specimen and no appreciable back reflection from the measuring instrument, then $J_5 = J_6 = J_8 = 0$, so that

$$J_2 = rI_2 \qquad I_5 = (1 - r)I_2$$
$$J_4 = rI_4 \qquad I_6 = (1 - r)I_4$$
$$J_7 = \sigma I_7 \quad \text{(in oil)}$$
$$\text{or } J_7 = S I_7 \quad \text{(in air)}$$

By a somewhat lengthy process of substitution for the various J_x in terms of I_x and progressive elimination the following intensity ratios are obtained as functions of r, ρ, θ and σ :-

$$\frac{I_6}{I_o} = \frac{\rho\theta(1-r)^2 \left\{ (1 - w\sigma)(r + w) + \sigma(1 - w)^2 \right\}}{M}$$

$$\frac{I_7}{I_o} = \frac{\theta(1-r)(1 - w)(1 + r^2\rho^2 - r^2\theta^2)}{M}$$

$$\frac{I_5}{I_6} = \frac{(1 - w\sigma)(1 - rw\rho^2 + rw\theta^2) + r\sigma(1 - w)^2(\theta^2 - \rho^2)}{N}$$

where

$$M = (1 - w\sigma) \left\{(1 - rw\rho^2 - r^2\theta^2)^2 - r^2\rho^2\theta^2(r + w)^2\right\}$$
$$- r\sigma(1 - w)^2 \left\{(1 - rw\rho^2 - r^2\theta^2)(\theta^2 + \rho^2) + 2r^2\rho^2\theta^2(r + w)\right\}$$
$$N = \theta \left\{(1 - w\sigma)(r + w) + \sigma(1 - w)^2\right\}$$

The second of these equations (I_7/I_o) is of use only when the specimen QQ is removed, when $\sigma = 0$, $w = r$ and the corresponding value I^1_7 can then be measured. The above equations then reduce to:-

$$\frac{I^1_6}{I_o} = \frac{2r\rho\theta(1 - r)^2}{(1 - r^2\rho^2 - r^2\theta^2)^2 - 4r^4\rho^2\theta^2}$$

$$\frac{I^1_7}{I_o} = \frac{\theta(1-r)^2(1+r^2\rho^2-r^2\theta^2)}{(1-r^2\rho^2-r^2\theta^2)^2-4r^4\rho^2\theta^2}$$

$$\frac{I^1_5}{I^1_6} = \frac{1-r^2\rho^2+r^2\theta^2}{2r\theta}$$

By elimination amongst these equations the following expressions for ρ, θ and r in terms of the observed intensity ratios are obtained:-

$$\rho = \frac{1}{W} + \frac{P}{2} \pm \sqrt{\frac{P^2}{4} + \frac{P}{W}}$$

$$\theta = \rho\sqrt{Z}$$

$$r = \frac{1}{W\rho}$$

where $X = \frac{I^1_5}{I^1_6}$ $\quad Y = \frac{I^1_7}{I^1_6}$ $\quad Z = \frac{Y^2-1}{X^2-1}$ $\quad W = X\sqrt{Z} + Y$

and $P = \frac{I^1_7}{I_o} \cdot \frac{\left\{\left(1 - \frac{1}{W^2} - \frac{Z}{W^2}\right)^2 - \frac{4Z}{W^4}\right\}}{\left(1 + \frac{1}{W^2} - \frac{Z}{W^2}\right) \cdot \sqrt{Z}}$

The required value, σ, of the reflectivity of the specimen in oil is now given by

$$\sigma = \frac{B - \frac{I_5}{I_6}D}{\frac{I_5}{I_6} - A}$$

where

$$A = \frac{r(1-w)^2(\theta^2-\rho^2) - w(1-rw\rho^2+rw\theta^2)}{\theta\left\{(1-w)^2 - w(r+w)\right\}}$$

$$B = \frac{1-rw\rho^2+rw\theta^2}{\theta\left\{(1-w)^2 - w(r+w)\right\}}$$

$$D = \frac{(r+w)}{(1-w)^2 - w(r+w)}$$

In these expressions, the value of w is calculated knowing r, and n, the refractive index of the immersion oil. For measurements in air, the above expressions can be simplified by writing $w = r$ and $\sigma = S$.

For the glass cube used in an experimental test of the method, r is about 0.04 and ρ and θ are about 0.5. It would seem therefore that terms in the foregoing equations involving r^4 will be negligible, and since $r^2\rho^2$ is almost equal to $r^2\theta^2$, the term $1 + r^2\rho^2 - r^2\theta^2$ will not differ significantly from unity. With these assumptions, the following simplified relationships hold:-

$$r = 1 + \frac{Q}{2} \pm \sqrt{\frac{Q^2}{4} + Q}$$

$$\theta = \frac{I_6^1}{I_5^1} \cdot \frac{1}{2r}$$

$$\rho = \frac{I_6^1}{I_7^1} \cdot \frac{1}{2r}$$

$$\text{where } Q = 2 \cdot \frac{I_7^1}{I_o} \cdot \frac{I_5^1}{I_6^1} \left[1 - \tfrac{1}{4} \left\{ \left(\frac{I_6^1}{I_7^1} \right) - \left(\frac{I_6^1}{I_5^1} \right)^2 \right\} \right]^2$$

and the reflectivity, S, of the specimen in air is then given by

$$S = \frac{B^1 - \frac{I_5}{I_6} D^1}{\frac{I_5}{I_6} - A^1}$$

$$\text{where } A^1 = \frac{r \left\{ (1 - r)^2(\theta^2 - \rho^2) - 1 \right\}}{\theta \left\{ (1 - r)^2 - 2r^2 \right\}}$$

$$B^1 = \frac{1}{\theta \left\{ (1 - r)^2 - 2r^2 \right\}}$$

$$D^1 = \frac{2r}{(1 - r)^2 - 2r^2}$$

The calculations for σ and S take approximately half and hour each on a desk calculator. In order to reduce the time taken for calculation and to avoid errors, a simple programme was written in 5 hole Algol for an Elliott 803 computer. The programmes for both σ and S are given in appendices 2 and 3 respectively.

Description of Apparatus

General description

The original apparatus used included the light source, spot galvanometer, photomultiplier and power pack described by Nichol (1962); but during the development of the apparatus several modifications in the stabilisation of the light source, measurement of the signal from the photomultiplier and photomultiplier divider chain were made. The apparatus here described was found experimentally to be the most suitable for this purpose (using the equipment available) and only the final apparatus which was used to measure all values quoted is described.

The apparatus (diagram 4) consists basically of a horizontal circle optical goniometer with a central stage supporting the glass cube with a semi-metallised diagonal. The specimen is supported on a second stage which can be placed in the light beam. Illumination was provided by a 48 watt car lamp; and an eleven stage photomultiplier was fitted over the viewing telescope to measure the intensity of light received. The signal from the photomultiplier was read from a digital voltmeter. In the following sub-sections details of the individual components are given.

Glass cube

The glass cube was made by Vickers Instruments Ltd., Haxby Road, York. It consists of two triangular prisms of borosilicate crown glass, and on the hypotenuse of one prism inconel (76% Ni, 15% Cr and 9% Fe), has been evaporated in vacuum. This is the same material as used by Hallimond (1957), for his standard surface. He gives the reflectivity of inconel as 51.8% at 589nm. The exact thickness of the inconel layer is not known, but during deposition its thickness is controlled photometrically and is thought to be of the order of 200 to 300 Å. The two glass triangles are cemented together with cellulose caprate leaving a layer of about 0.5 mm thickness with a refractive index of 1.49. The completed glass cube was 17 mm square with a semi-metallised diagonal. An outline of the evaporation technique used for metallising is given by Holland (1960).

Because the geometry of the cube is so critical, the interfacial angles were measured using the optical goniometer, with the following results:-

Face	Angle	Difference
1	$211^{\circ}19' \pm 1'$	
2	$361^{\circ}24' \pm 1'$	$90^{\circ}05'$
3	$31^{\circ}30' \pm 1'$	$90^{\circ}06'$
4	$121^{\circ}23' \pm 1'$	$89^{\circ}53'$
1	$211^{\circ}18' \pm 1'$	$89^{\circ}55'$

It can be seen that the maximum departure from 90° is 7'.

The refractive index of the glass cube was measured at different wavelengths with an Abbé refractometer using a continuous band interference filter monochromator. The results were as follows:-

Wave length (nm)	Refractive index
620 (red)	1.509 ± 0.001
589	1.509 ± 0.001
546	1.509 ± 0.001
500	1.509 ± 0.001
470 (blue)	1.510 ± 0.001

The calculated reflectivity of the cube is 4.12% in air at 589nm.

Goniometer

The goniometer, (No. 3029), was made by Unicam Instruments Ltd., Cambridge. It has a fixed collimator causing the incident light to be parallel; a travelling telescope which can be moved in and out and also around the goniometer on a scale calibrated in one minute intervals, and a stage that supports the glass cube that can be rotated in the horizontal plane, moved in two directions in the horizontal plane and rotated in the vertical plane by two arcs at right angles. The travelling telescope has a lens which can be put in place, so that the telescope acts as a microscope.

The specimen was supported on the adjustable arcs taken from a Philips Universal Flat Plate X-ray camera to allow the necessary orientation relative to the light beam.

The photomultiplier and power pack

The photomultiplier, an E.M.I., eleven stage, type 6094B was the same as used by Nichol (1962) except for modifications to the divider chain. The photomultiplier has a Kodial window glass fifty one centimetres in diameter, and a cathode diameter of ten centimetres. The cathode is Cs-Sb with a wavelength range of three thousand to six thousand angstroms (diagram 6). Its average photosensitivity under typical conditions is given by the manufacturers as 50 uA/L, and its minimum photosensitivity is 30 uA/L. The photomultiplier was mounted in a light tight brass case with a camera shutter in front of the cathode, and was supplied with 150 volts per stage.

The power for the photomultiplier was supplied by a "Cintel" stabilised E.H.T. power pack type 2000/5, made by Cinema-Television Ltd., Worsley Bridge Road, Lower Sydenham, London, S.E.26. The instrument has a continuous voltage range from 500 to 2000 volts with a maximum output current of 5 mA, and according to the makers' specifications, the ratio of input voltage change/output voltage change is better than one hundred to one. This stability was checked using a digital voltmeter and found to be as the manufacturers stipulated.

It was noted that there was a marked variation in the output from the photomultiplier across its cathode, as demonstrated by Edels and Ganbling (1957). For any one set of readings therefore, the photomultiplier was clamped firmly in position.

Digital voltmeter

Because of the increased speed and accuracy in using such a device, when the digital voltmeter became available, it was employed to read the output from the photomultiplier.

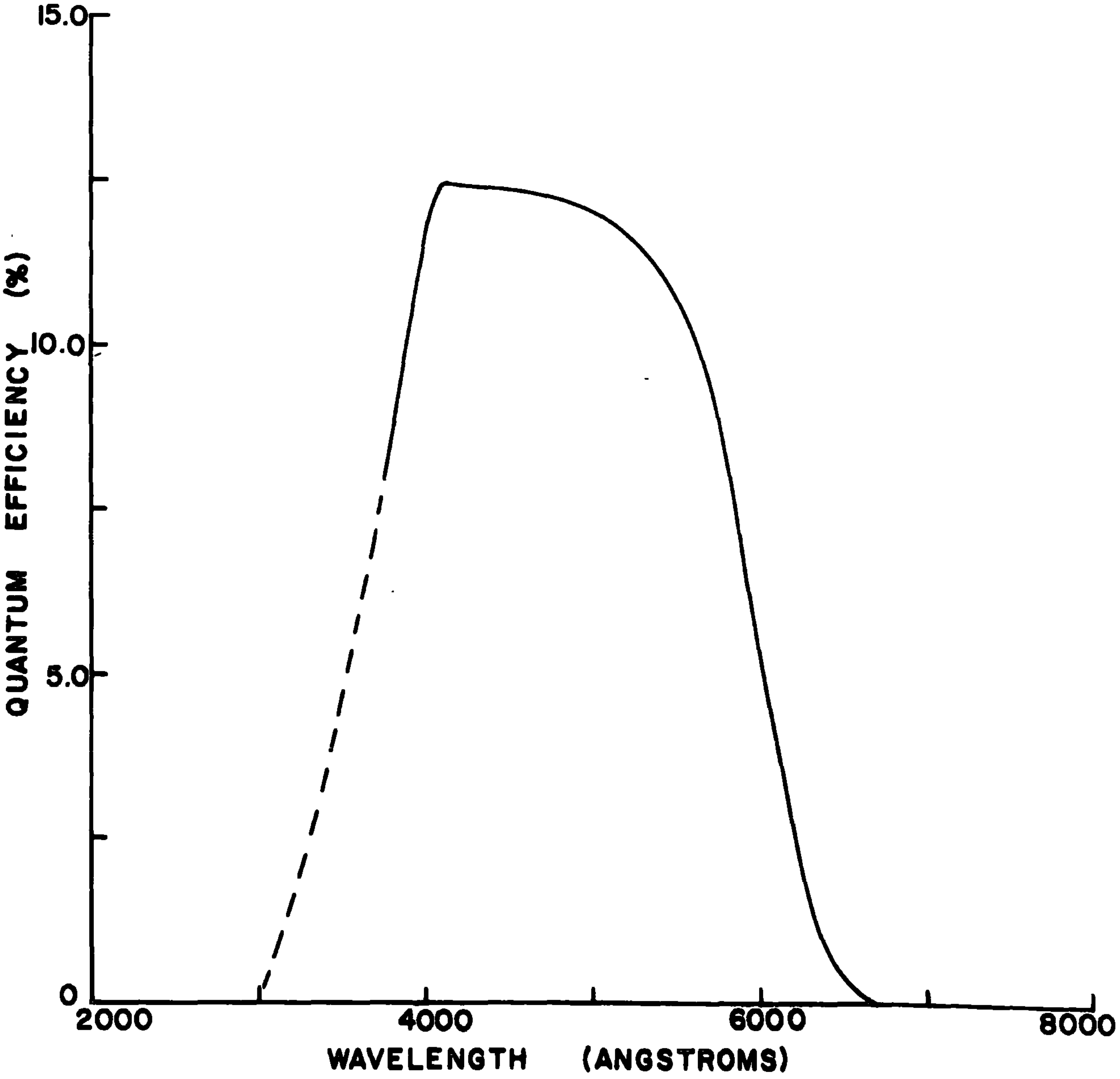


DIAGRAM 6 WAVELENGTH RANGE OF THE PHOTOMULTIPLIER, E.M.I. 6094B

The voltmeter was of the high impedence type, made by Digital Measurements Ltd., (DM2005) and with suitable use of the scale selector recorded the voltage once every millisecond to four significant figures. The voltage was measured across a 1 megohm resistor, as shown in diagram 7.

Potential divider for the photomultiplier

In order to get maximum linearity and highest stability of gain under D.C. conditions, according to the makers' specifications, the anode current should not be allowed to exceed 10 microamperes and the current down the divider chain should be at least 10 times the current down the anode chain. The divider chain was constructed using a 100 k ohm Farnel Instruments Ltd. "high stab" resistor per stage, giving a divider chain current of 2 milliamperes and a potential of 150 volts per stage. The anode current was restricted to 10 microamperes by the use of the optical attenuator described in the section on linearity, although, according to the manufacturers (E.M. Worster, E.M.I. Valve Sales Division, personal communication) with a dynode chain-current as high as 2 milliamperes an anode chain current of about 100 microamperes or even higher should be tolerated before instability or non-linearity resulted. This would still mean that the dynode chain current was more than 100 times the anode chain current. The possibility of using this facility to improve the precision of the reflectivity results is discussed later.

Linearity of the photomultiplier

A check of the linearity of the photomultiplier used was carried out by Nichol (1962) using a series of neutral density filters of varying transmission and it was concluded that the device showed adequate linearity. More recently, in discussions and personal communications (R. Phillips and E.N. Cameron) some doubts have been expressed as to the adequacy of the linear response and so it was decided that this would be tested more thoroughly. It was suggested, (R. Phillips, personal communication), that the simplest method for producing accurately known

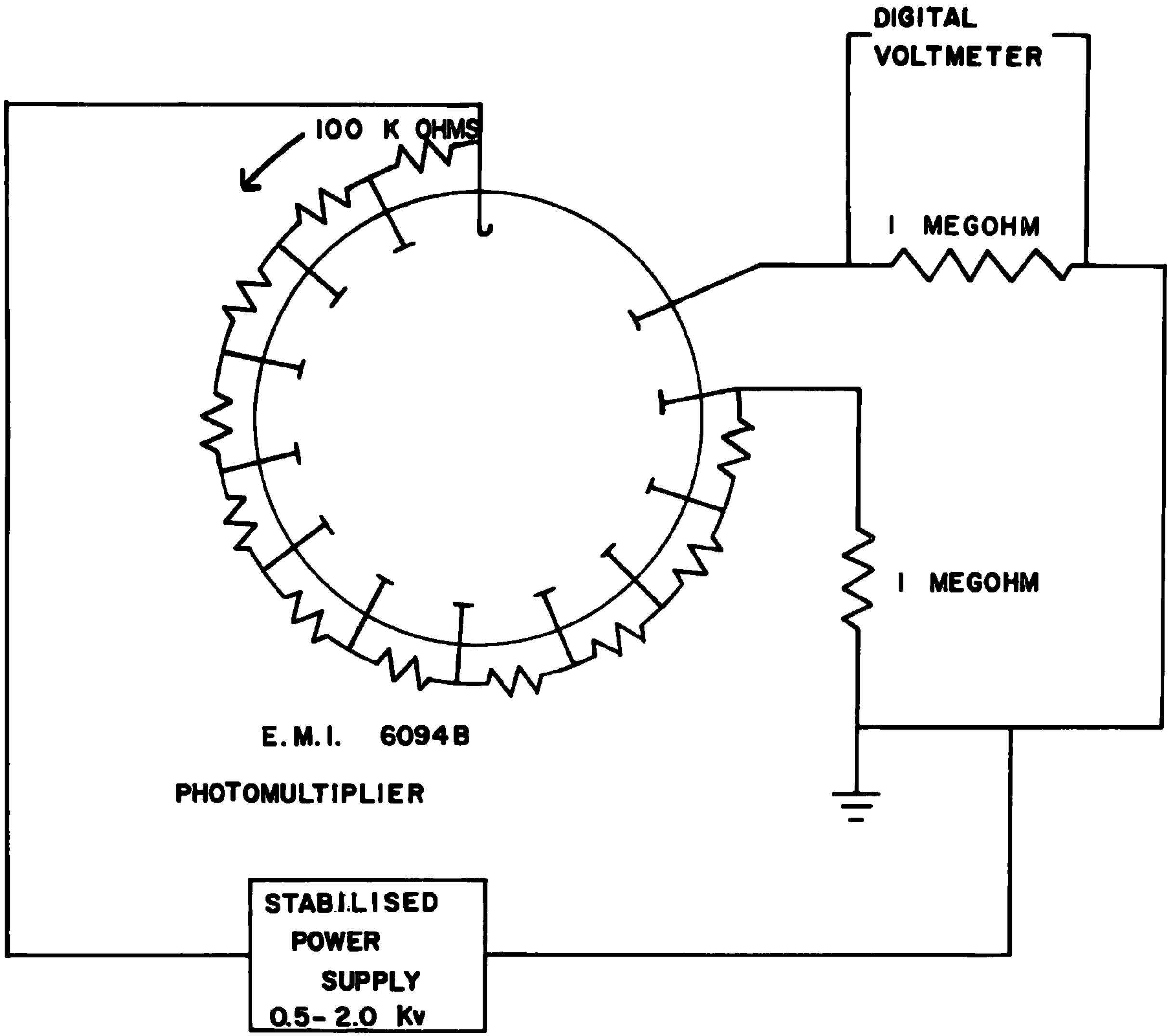


DIAGRAM 7 CIRCUIT DIAGRAM FOR THE PHOTOMULTIPLIER

ratios of light intensity would be to insert a pair of polarising filters into a light beam and vary the angle of uncrossing.

A perfect polar may be defined as a device which from a beam of non-polarised light can produce a beam of plane polarised light vibrating in one single direction, the permitted vibration direction, with zero intensity for vibration in any other direction. It is easily shown that after passing through two perfect polars, the intensity of the resultant plane polarised beam is proportional to $\sin^2\theta$, where θ is the angle of uncrossing of the polars, that is, the complement of the angle between the permitted vibration directions. Thus, a pair of perfect polars would form a simple optical attenuator providing known ratios of light intensity by varying θ, and the readings of a perfectly linear detector plotted against $\sin^2\theta$ would be a straight line. In practice, however, a polarising filter is not a perfect polar, since there is a measurable transmission of light even when two filters are exactly crossed, and this varies with wavelength. Whatever the vibration direction of a given element of the transmitted light, it may be considered in terms of two components vibrating respectively parallel and at right angles to the permitted vibration directions. The amplitude of the parallel component will be very much larger than that of the other component, the exact ratio depending on the quality of the polarising filter. Because of the birefringent nature of the filter, there will also in general be a phase difference between the two components, but because of the large difference in amplitudes the resulting ellipticity will be small. If $A = A_o \sin wt$ is the amplitude of the light vibration in a given direction entering the first polar, this is resolved into components $P = A_o(.\sin\alpha)\sin wt$

and $S = A_o(.\cos\alpha)\sin wt$

respectively parallel and perpendicular to the permitted vibration direction, which forms an angle $(90-\alpha)$ with the original vibration direction. On leaving the first polar each of these amplitudes has been reduced by absorption and a phase difference has been introduced due to the birefringence. Thus the amplitudes of the two components entering the second polar will be $P_1 = x\ A_o(\sin\alpha)\sin(wt + \delta)$

$S_1 = y\ A_o(.\cos\alpha)\sin wt$

where x and y are the transmission fractions for the two directions and δ is the phase angle.

For the components leaving the second polar we then have

$$P_2 = x^2 A_0 \sin\alpha\,(\sin\theta).\sin(wt + 2\delta) + xyA_0\cos\alpha\,(\cos\theta).\sin(wt + \delta)$$

$$S_2 = xyA_0\sin\alpha\,(\cos\theta).\sin(wt + \delta) - y^2A_0\cos\alpha\,(.\sin\theta).\sin wt$$

By a slightly tedious calculation it can be shown that the expression for the resultant intensity in addition to a term in $\sin^2\theta$ also contains a term in $\sin 2\theta$ and a constant.

It is now necessary to consider the effect on this expression of an error in determining the exact crossed position of the polars. The position is found by determining the setting of the polars for which the intensity is a minimum. In addition to the error in determining very low intensities the rate of change of intensity with angle of uncrossing decreases as the crossed position is reached, giving a very flat curve, so that an error is almost unavoidable. If readings are taken for a complete rotation of one polaroid, and angle of $+ \epsilon^{\circ}$ from the assumed crossed position will actually be $(\epsilon + \delta\theta)$ degrees, where $\delta\theta$ is the difference between the true and assumed crossed positions. Similarly an angle $-\epsilon^{\circ}$ will be $(\epsilon - \delta\theta)$ degrees. If the photomultiplier output current is linear with respect to light intensity and the voltage V developed across a resistance in the anode circuit is measured, it can be shown that $\bar{V}$, the mean of the voltages measured for the above two angles, is given by

$$\bar{V} = a + b\sin\epsilon\cos\epsilon + c\sin^2\epsilon$$

Where ϵ is the angle of rotation from the assumed crossed position, and a, b, c are constants. The voltage values must of course be corrected for photomultiplier dark current. Thus even with a perfectly linear photomultiplier response, a plot of $\bar{V}$ against $\sin^2\theta$ may not give the straight line which is suggested by the usual theoretical treatment.

The E.M.I. 6094B eleven stage photomultiplier used by Nichol (1962) was tested for linearity using essentially the same experimental arrangements as in the earlier work. The light source was supplied from an electronically stabilised power unit, Farnell Instruments Ltd., TSV70, instead of the heavy duty accumulators originally used. After passing through a continuous band interference filter monochromator, the light beam traversed a polaroid screen held on a microscope stage, then a fixed polaroid before entering the photomultiplier. The galvanometer originally used was replaced by a 15,000 ohm resistor and the voltage developed across this was measured with an accurate potentiometer (W.G. Pye & Co. Ltd.).

The results obtained were checked by a method of least squares and it was found that a standard deviation of 0.008 of a volt for readings between 0.012 and 0.340 volts occurred. In attempting to reduce this level of error, the circuit was checked in detail and it was found that an internal short circuit had developed in the photomultiplier between two of the dynodes due to sagging of one of the internal elements. The photomultiplier was thus acting as a nine stage device with an attendant loss of stability and gain. This experience suggests that careful checking is required for photomultipliers which have been in use for an extended period if measurements of high accuracy are required, since there was no obvious change in the characteristics of the circuit when used for routine measurements. The damage to the apparatus had almost certainly occurred during movement to a new location some time after the original work of Nichol (1962). A replacement photomultiplier of the same type was obtained and the opportunity was taken to alter the characteristics of the dynode chain as already outlined. In addition the signal from the photomultiplier was measured with the digital voltmeter described in the last section.

For light of 589 nm measurements were made at 10° intervals of θ for 2 complete rotations of the movable polaroid. The results for each complete rotation were averaged on either side of the assumed zero position, i.e. 10° and 350°, 20° and 340° etc. leaving 2 complete sets of results from 10° to 180°, and these were then averaged further using the two 10° and two 170° results giving an average of 8 readings for every 10° from 0° to 90°. The averaged results were fitted by the same method of least squares using the Algol programme on the Elliott 803 computer (the programme is given in appendix 4).

From table 1 which gives the residuals of the regression plus the standard deviation of $\bar{v}$, a, b and c it is evident that the residuals are all of the same magnitude, and that the standard deviation of $\bar{v}$ is about 0.1. Also it was found that c is the largest constant and has a low standard deviation and therefore accounts for a very high proportion of the regression, b is an order of magnitude smaller than c and has a moderate standard deviation, while a is an order of magnitude smaller than b and although showing a negative intercept has such a large standard deviation that this figure can only be taken as an order of magnitude. As the voltages measured varied from 0.54 to 15.8 a standard deviation of 0.1 volt gives a large percentage error in the lower range but very moderate error in the higher range. As the voltage was measured across a 1 megohm resistor the left hand column in table 1 can also be read as microamperes, which means that at higher angles the manufacturers maximum recommended anode current of 10 uA has been exceeded. If only the readings below 10 uA are included in the regression the results are as shown in table 2. The standard deviation of $\bar{v}$ is now an order of magnitude smaller, i.e. about 0.01 volts.

The effect of these standard deviations and residuals is discussed under the section on "Precision of Measurements".

Table 1

Linearity of the photomultiplier (total)

a = −0.1963

b = 1.1295

c = 16.0145

Standard deviation of $\bar{v}$ = 0.0637

Standard deviation of a = 0.0679

Standard deviation of b = 0.1393

Standard deviation of c = 0.0640

Voltage (observed)	θ (degrees)	Residual
0.5380	10.0	0.0582
2.0200	20.0	−0.0201
4.2610	30.0	−0.0354
6.9200	40.0	−0.0567
9.7400	50.0	−0.0180
12.4000	60.0	0.0963
14.3600	70.0	0.0521
15.4700	80.0	−0.0585
15.8000	90.0	−0.0183

Table 2

Linearity of the photomultiplier using all Readings Below 10 uA

$a = -0.0534$

$b = 0.5864$

$c = 16.1946$

Standard deviation of $\bar{v}$ = 0.0117

Standard deviation of a = 0.0234

Standard deviation of b = 0.0937

Standard deviation of c = 0.0572

Voltage (observed)	θ (degrees)	Residual
0.5380	10.0	0.5260
2.0200	20.0	-0.4673
4.2610	30.0	0.2783
6.9200	40.0	-0.0945
9.7400	50.0	0.0132

Optics

The optics were designed to give a small beam of perfectly parallel plane polarised monochromatic light by the system shown in figure 3.

The lamp was mounted in an adjustable holder, with condenser and diaphragm, of the type often used in ore microscopy. The lamp condenser was adjusted to focus the lamp filament at infinity, and the lamp iris was closed to its smallest aperture (about 2 mm). The light beam next passed through the interference filter and then through a polaroid which could be rotated through 360° (and also form an optical attentuator to control light intensity) and through a second polaroid with its vibration plane vertical. The light beam then passed through the object slit which was formed by crossing two razor blades to form a diamond about 0.25 mm across the diagonal. With the aid of the plano-convex image lens the light beam was focused on the back lens of the telescope so that it appeared in focus to the observer. The light beam passed through the glass cube and into the telescope lens or onto the specimen if it was in place. The optics of the telescope are such that the eye-piece can be moved to focus the telescope at infinity, and with it in this position and the image lens as already described, an enlarged image (about 2mm across the diagonal measured at the telescope eye-piece) of the object slit is seen in focus. A diaphragm with a 5 mm diameter aperture was placed in the telescope to reduce the effect of multiple reflections, and crossed hairs were placed in the centre of the diaphragm to help in locating the image in exactly the same position each time. In order to reduce the fatigue of the photomultiplier cathode due to excessively intense light (see Kenne, 1963 for a discussion of this effect) and also to reduce the effect of variation of sensitivity across the surface of the photomultiplier, a frosted glass was placed directly in front of the photomultiplier window to diffuse the light over the whole surface.

Interference filter

The interference filter (no. 544007) was the continuous band type originally designed by the Atomic Energy Division of the Geological Survey of Great Britain and described by Harrison and Day (1963). Throughout all experiments the half height band width, according to the makers calibration, was about 25nm.

Stabilised light source

Illumination was provided by a 12 volt 48 watt compact filament car lamp, the power to which was supplied by a Farnell TSV70 stabilised power supply. The stabilisation ratio of the power supply was tested using the digital voltmeter and found to be well within the stabilisation ratio of 2000:1 claimed by the manufacturers.

Procedure

The light source and the photomultiplier were turned on and the system allowed to come to equilibrium forty-eight hours before any readings were taken. The lamp condenser was adjusted until the image of the lamp filament was focused at infinity, and the telescope eye-piece was altered until the telescope was focused on infinity. The image lens was then altered until the object slit was in focus to the observer. The lamp iris was closed to its smallest aperture (about 2 mm in diameter) so that only the central part, and therefore the most parallel part of the light beam was used. With the microscope lens of the telescope in place, it is possible to see the lamp iris and lamp filament, and so careful adjustment was made until the two were in direct line with the axis of the telescope. The continuous band type interference filter was put in place in front of the lamp and a polaroid, with its vibration direction vertical, was placed in front of the interference filter. The glass cube was put on the stage and the height and horizontal movement of the stage altered until the cube was central, in which position it entirely filled the field of view. All this was possible by looking through the microscope lens. If the cube is placed with the semi-metallised diagonal exactly parallel to one of the arcs with vertical movement, this helps subsequent adjustment. With the microscope lens out of position the telescope was lined up exactly with the incident beam, and the vernier scale adjusted to one hundred and eighty degrees precisely. The telescope was then turned to the 90° position. With the help of the horizontal and vertical movements, the glass cube was altered until the reflection of the image from the semi-metallised diagonal was exactly central. To make sure that the cube is truly level, the telescope is turned to 270° and with the aid of the vertical arc movement which is at right angles to the semi-metallised diagonal, the reflection of the image from the appropriate face is centred. If the centring is carried out in this manner the cube is perfectly level and the diagonal is exactly at 45° to the incident beam.

With the telescope still at 270° position the specimen was supported on its stage at the 90° position, and placing the specimen about one millimetre from the glass cube, the specimen was positioned until its image was exactly centred. The photomultiplier was then fitted over the telescope eye-piece, and the two readings with the specimen in place were taken followed by the three readings taken without the specimen in place. The exact positioning of the telescope for each reading was achieved by using the 360° scale and vernier.

For each set of readings great care was taken in blacking out the room and in shielding all internal light sources.

Results

Owing to the development of the fault in the first photomultiplier necessitating its replacement, the earlier results were erratic, and after replacment of the photomultiplier there was not sufficient time to make any very large number of observations. All values quoted in table 3 were calculated from measurements taken at 589nm in air with the new photomultiplier. The recommended values for the reflectivity of the samples are taken, in the case of silicon, from data supplied with the specimen by E.N. Cameron; the exact reflectivity value for silicon is in doubt as H. Piller (personal communication) also measured a sample and got a slightly lower value than Cameron. The pyrite was supplied by S.H.U. Bowie and is from the Elba. There is some variation in the literature concerning the reflectivity values for pyrite; Bowie et al, (1965),

Table 3

Reflectivity Results (in air)

All measurements made at 589 nm.

Date and number	Specimen	ρ %	θ	r%	S%	Rec. S(%)	S.E.
April 21st No.2	Silica *	32.3	16.9	5.23	37.3	36.3	
" " No.3	"	32.1	15.2	4.72	41.4	"	
" " No.4	"	33.2	15.4	4.80	37.7	"	
April 22nd No.1	"	33.9	12.9	5.43	40.7	"	
" " No.2	"	33.6	14.7	4.84	37.7	"	
" " No.3	"	33.4	14.2	5.09	39.2	"	0.79
" " No.4	"	33.8	14.9	4.56	39.7	"	
" " No.5	"	33.9	14.0	4.94	37.5	"	
April 26th No.1	"	31.6	15.9	5.04	34.3	"	
" " No.2	"	33.9	14.4	5.79	33.2	"	
" " No.3	"	33.7	14.4	5.27	40.6	"	
" " No.4	"	34.1	14.3	5.61	42.1		
				average	38.4		
April 22nd No.6	Pyrite**	33.7	14.9	4.67	57.4	54.4-55.0***	
" " No.7	"	33.7	15.0	4.98	58.0	"	
April 23rd No.1	"	33.4	15.0	4.80	56.7	"	1.08
" " No.2	"	33.3	14.8	5.00	54.9	"	
" " No.3	"	33.8	11.0	5.50	52.0	"	
				average	55.8		

Table 3 (continued)

*A pure single crystal of silicon grown in the laboratory and supplied by E.N. Cameron.

** Pyrite from the Isle of Elba supplied by S.H.U. Bowie.

*** See the discussion in the body of the paper for the exact value.

Rec. = recommended value for S.

S.E. = Standard Error.

quotes the reflectivity of two specimens of pyrite from Elba measured by the National Physical Laboratory as 55.0 and 54.4 respectively at 589.3 nm, this agrees quite well with values quoted by Hallimond, (1957), of 54.3 at 580 nm, and 55.1 at 610 nm, (giving a value of 54.5 at 589 nm by extrapolation). Using the same specimen of pyrite as employed during these measurements, Hallimond's apparatus and a marmatite standard, Nichol, (1962), measured the reflectivity as 54.5 at 580 nm, and as 55.4 at 610 nm giving by extrapolation 54.8 at 589 nm. It appears that 54.8 is the most probable value of the reflectivity at 589 nm for this particular specimen of pyrite.

Although there was insufficient time to repeat the measurements in oil with the new photomultiplier, several measurements had already been made with the old tube. These results are erratic and lack accuracy but they do demonstrate the possibility of making such measurements and are included for that reason. The results are quoted in table 4. The recommended values for both the refractive index and absorption constant are taken from Wooster, (1957).

Table 4

Measurement of n and K

All measurements were made at 589 nm using an oil of refractive index 1.5100. The reflectivity of pyrite in air was taken to be 54.8% and the reflectivity of the glass cube in oil, (0.026%) was calculated knowing the refractive index of both the glass cube abd the oil

Date and number	Specimen	n	recommended n	K	recommended K
Oct.30th No. 4	Pyrite	0.494	3.07	1.02	0.91
" No. 5	"	0.746	"	0.34	"
" No. 6	"	0.418	"	1.39	"
	average	0.453	average	0.92	

Precision of Measurements

Errors due to fluctuations in the photomultiplier current

Although the digital voltmeter recorded to 4 significant figures, it was found that, especially for the lower light intensities, there was sufficient variability in the photomultiplier current to make readings to this accuracy unreliable. Although the fourth significant figure was sometimes estimated, the results quoted are generally only accurate to ± 1 in the third significant figure and are very seldom worse than ± 2.

Errors due to mis-setting of the goniometer

It was found experimentally, that with the frosted glass in place in front of the telescope eye-piece small errors (i.e. up to 3') in the setting of the goniometer caused negligible variation in the photomultiplier current, while greater errors in the goniometer setting caused a very large variation. Because the goniometer is calibrated in 1 minute intervals it can be set to ± 1 minute and so errors from this cause will be negligible.

Errors due to drift in the power supplies

Including any drift in the power supply to the photomultiplier or lamp the photomultiplier was still found linear within the limits already stated. As measurement of the photomultiplier linearity data took an hour and each measurement of reflectivity takes only 20 minutes any effect due to drift should be included in the linearity data.

Errors in the linearity of the photomultiplier

The linearity of the photomultiplier has already been discussed in detail and it was shown that the largest standard deviation was about 0.1 volts, while the standard deviation for readings below 10 uA was about 0.01volts. This error exceeds all other errors by an order of magnitude and is therefore the one which will be largely responsible for errors in the calculation of reflectivity.

Total error

While errors due to the mis-setting of the specimen or the glass cube, and other such errors cannot be determined, it is assumed that such errors are random and will only appear, if care is used, as fairly large errors in occasional observations and so could be detected and neglected.

The main source of error in the value for reflectivity (in either air or oil) is due to errors in measuring the photomultiplier current and normally errors of ± 0.01 volts can be expected, but errors as high as 0.1 volts are possible.

Because of the complexity of the equations for the calculation of σ and S, it was found easiest to assess the error in the final values calculated due to errors in the initial observations by taking a set of results, changing each observation in turn, computing the answer, and observing the resultant change in e, Θ, r and S (or σ). Table 5 shows the resultant change in these values for a change of + 0.01 volts in each observation taken individually.

Table 6 shows the resultant change in e, Θ, r and S when each observation is changed by ± 0.01, in such a manner that in each case an increase in S resulted. The final figure shows the largest possible percentage error in S that could result from an error of ± 0.01 volts in all observations (under the same conditions as the original readings were made).

The calculated error of 18% for S, shown in table 6, is found to be considerably higher than the variation about the mean of the results quoted in table 3 as the maximum error is 13% and the standard error ABOUT
1.08%? 10%. This suggests that the errors are not as the maximum calculated, and that, with the present experimental arrangement, 95% of the results will fall within ± 10% of the mean.

From curves given by Piller and Gehlen (1964), it can be seen that errors of 10% in both the reflectivity in oil and air will cause errors as large as an order of magnitude in the calculated values of the refractive index and absorption constant. So, although values for n and K can be calculated from the present results the errors are so large as to make the values meaningless.

Table 5

Changes in e, θ, r and S (shown as a percentage) due to errors of + 0.01 of a volt in each experimental observation.

Initial Observation	Resultant change in:-			
	e(%)	θ(%)	r(%)	S(%)
Io = 8.99	-0.1	-0.1	+0.1	+0.1
$I'_5 = 1.04$	-0.1	+0.9	-0.8	+0.3
$I'_6 = 0.0383$	+2.7	+2.6	+22.9	-7.8
$I'_7 = 2.73$	+0.3	0.00	-0.3	-3.4
$I_5 = 1.02$	0.00	0.00	0.00	-1.2
$I_6 = 0.166$	0.00	0.00	0.00	+7.6

Table 6

Changes in e, θ, r and S due to errors of ± .01 volts in the initial observations (errors were chosen as either + or - so that in each case they would give a positive error in S)

Initial observations	Change	Observations used for computation
$I_0 = 8.99$	+0.01	9.00
$I_5' = 1.04$	+0.01	1.05
$I_6' = 0.0383$	-0.01	0.0283
$I_7' = 2.73$	-0.01	2.72
$I_5 = 1.02$	-0.01	1.01
$I_6 = 0.166$	+0.01	0.176

Initial Result	Final Result	Percent Change
$e = 0.3394$	0.3285	3.2
$\theta = 0.1292$	0.1268	1.9
$r = 0.05427$	0.04102	24.4
$S = 0.4069$	0.4790	17.8%

Conclusions and Critical Discussion

While the precision of the reflectivity results obtained is low and a little disappointing, all the results fall within the limits of error calculated. It is felt that results are sufficiently accurate to show that the theory of the method is correct, and the fact that all the error can be accounted for demonstrates that only improvements in the instrumentation are required. The possibility of such improvements is discussed in the section titled "Recommendations".

The advantages of this method are that it has been shown to have the potential of removing several drawbacks found in most methods used for determining reflectivity. Perhaps the biggest drawback to reflectivity work so far, is the lack of suitable standards. The difficulties here have already been discussed, but the fact still remains that until there is a standard, or standards, which can be kept in any laboratory, and which will last for some time, the exact measurement, and more important the exact comparison of reflectivities between workers, will be uncertain.

Another inaccuracy inherent in most systems so far discussed, is the convergence of light from the microscope lens onto the specimen. It has been shown that the greater the numerical aperture, the greater the difference of the reflectivity with respect to measurements made at supposed normal incidence. As already stated, Berek, (1953), found a minimum error of 1.25% between objectives with numerical apertures of 0.1 and 0.3 respectively. So, although the convergence of light can be ignored to the first approximation, for accurate results, this error must be considered.

Cambon (1949), discussed the rotation of polarised light due to reflection from the microscope illuminator. It can be seen on examining any isotropic section that the field is not uniform, but gets lighter towards the edges, i.e., the rotation of the polarised beam increases towards the edge of the field. Although this effect can be reduced by using only the central part of the beam, it is still present. Polarised light is better than non-polarised light in this respect but there is still an error which reduces the accuracy of the results. In the system employed here, the absence of an illuminator avoids this problem.

Yet another drawback to all presently available methods for determining reflectivity is the difficulty in measuring the reflectivity in oil, and so determining the refractive index and absorption constant. While the errors in determining the reflectivities are too large as yet to make reliable estimates of the refractive index and absorption constant, it is felt that the possibility of measuring the reflectivity in oil has been demonstrated.

In spite of the low precision reported in these initial results it is hoped that the advantages of getting an absolute determination of the reflectivity of an opaque substance in perfectly parallel plane polarised light which has undergone no rotation, coupled with the possibility of making measurements in both air and oil will prove this to be a worthwhile method and that it will be possible to undertake further work to improve the precision.

Recommendations

The apparatus as used was found to be satisfactory in most respects; such variables as the geometry of the glass cube and stabilisation of the light source and power pack for the photomultiplier were determined independently and found to be well within the usable limits. However, there are still several modifications which should be made to the apparatus in order to get maximum stability and accuracy. These are dealt with in turn.

The specimen support

While the adjustable arcs already described were ideal for supporting the specimen, the arcs themselves were only suspended (upside down) from two steel rods which in turn were held by retort stands. It was observed that any small pressure on the table in the region of the apparatus caused a small movement of the specimen during measurement.

Integrating sphere

The problem of non-uniformity of response of the photomultiplier cathode and fatigue due to too intense illumination has already been mentioned. Both these problems could probably be completely overcome by the use of an integrating sphere of the type used by the National Physical Laboratory during their measurments of reflectivity. A full description of the construction and use of integrating spheres is given by Walsh (1958, pp.257-283).

An integrating sphere, 4 inches in diameter, was constructed using a commercially available white base coat and white matt finish with a reflection factor of 0.90 (available from the Indestructible Paint Company Limited, Whitby Avenue, London, N.W.10). However, it was found that the sphere caused a reduction in light intensity of about 50 times and this resulted in an intensity too small to give sufficient response from the photomultiplier. However, the stabilised power supply for the lamp is capable of 350 watts, and if the present 48 watt lamp were replaced with a larger one, sufficient illumination should be available.

Stability of the photomultiplier

As evidenced by the fluctuations shown in the digital voltmeter readings there is a measurable variation in the current from the photomultiplier. If the photomultiplier case could be brought to earth potential without disturbing the space charge within the case, a steadier current should result and readings could then be taken with greater precision. If the current was sufficiently stabilised to make measurements to four significant figures possible a large increase in precision could result.

More important, a steadier current from the photomultiplier should result in a lower standard deviation of the linearity measurements and hence greater accuracy in all measurements. However, a source of inaccuracy greater than any departures from linearity of the photomultiplier is the very low voltages being used with a subsequent large percentage error. The manufacturers state that the anode current should be no more than 1/10th of the dynode current, which means that a maximum current of 200 uA should be possible in spite of the 10uA restriction normally placed on the anode current. As already discussed (see the section on the photomultiplier), and as evidenced by the results in table 5, the photomultiplier should still be just as linear well above 10 uA if the readings at lower currents could be avoided. Consequently, if a more intense light source is used so that the lowest voltage is a factor of 10 higher, a reduction in the reading errors of an order of magnitude should result.

Errors of such a magnitude would also make possible a reasonably accurate estimate of the absorption constant and refractive index.

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* Denotes references which have not yet been examined by the writer, the data referred to in these references being taken from papers by later authors.

Appendix I

The spot galvanometer - linearity and scale relationships

For early measurements of the signal from the photomultiplier the same galvanometer as employed by Nichol (1962) was used. Because of the wide range of output signals measured, it was found necessary to check the linearity and scale relationships. Although the galvanometer was not used for the final measurements quoted, the data on linearity is included here as it may be of use to other workers.

The galvanometer used was a "spot galvanometer" made by Cambridge Instrument Co. Ltd., No. 351528, having a 450 ohm internal resistance and fitted with a direct and a times 1, 1/10th, 1/100th and 1/1000th scale. The scale, which is 160 millimetres long, is divided into one hundred divisions and there is a centring device so that the rest position of the spot can be altered. On its most sensitive range (times 1), a deflection of 170 millimetres is given by 1 uA, therefore a full scale deflection represents 0.94 uA on the times 1 scale, 9.4 uA on the times 1/10th scale etc.

The linearity of the galvanometer was checked, first of all on the times 1/10th scale, and then the relationship between the times 1/10th and times 1, 1/100th and 1/1000th scales was determined. The results are reproduced in appendix one. It was found that, provided no readings are taken below twenty scale divisions, including reading errors, the galvanometer is linear to within 1.5% on the 1/10th scale, between any two readings. The times 1 and 1/100th scales were found to differ from the 1/10th scale by less than 1/2% while the 1/1000th scale differs by 1%. Because of the close agreement between the different scales, it was assumed that they are all linear to the same degree as the 1/10th scale, i.e. 1.5%.

Figure 1 shows the circuit used during the reflectivity readings. It will be noted that the internal resistance of the galvanometer (Rg), changes from 450 to 45 to 4.5 to 0.45 ohms as the scale changes from 1 to 1/10th to 1/100th to 1/1000th respectively. However, because the change in resistance is small compared with the four megohm resistance in the circuit (i.e. about 0.5%) its effect can be neglected for the purposes of this experiment.

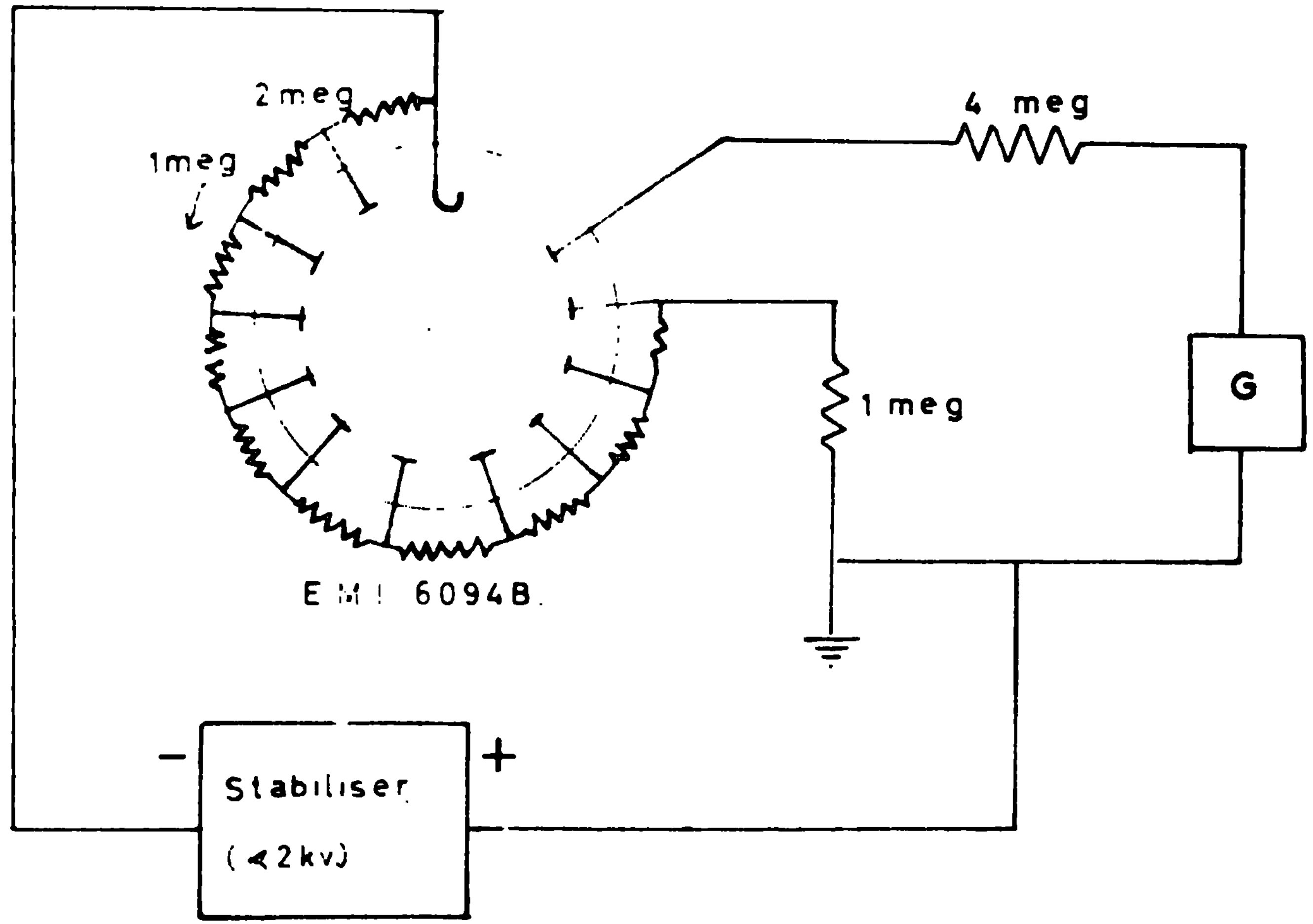

FIG 1 CIRCUIT DIAGRAM FOR REFLECTIVITY MEASUREMENTS.

Part I: To determine the linearity of the galvanometer

The circuit shown in figure 2 (appendix I) was constructed using the galvanometer, a "standard battery" with 7 positions of known E.M.F., and a fixed, wire resistor of 10^6 ohms. The galvanometer reading was taken for different E.M.F.s and a direct comparison made.

The results obtained were:-

Voltage V volts	Divisions D divisions x 10	$\frac{\text{Voltage - Divisions}}{\text{Voltage}} \times 100$ $\frac{V - D}{V} \times 100$ percent
1.35	1.30	4.0
2.70	2.70	0.0
4.05	4.03	0.5
5.40	5.32	1.5
6.75	6.64	1.6
8.10	7.99	1.4
9.45	9.32	1.4

Provided that no reading is taken below 20 scale divisions, the galvanometer is linear to ± 1½% on the 1/10th scale between any two readings.

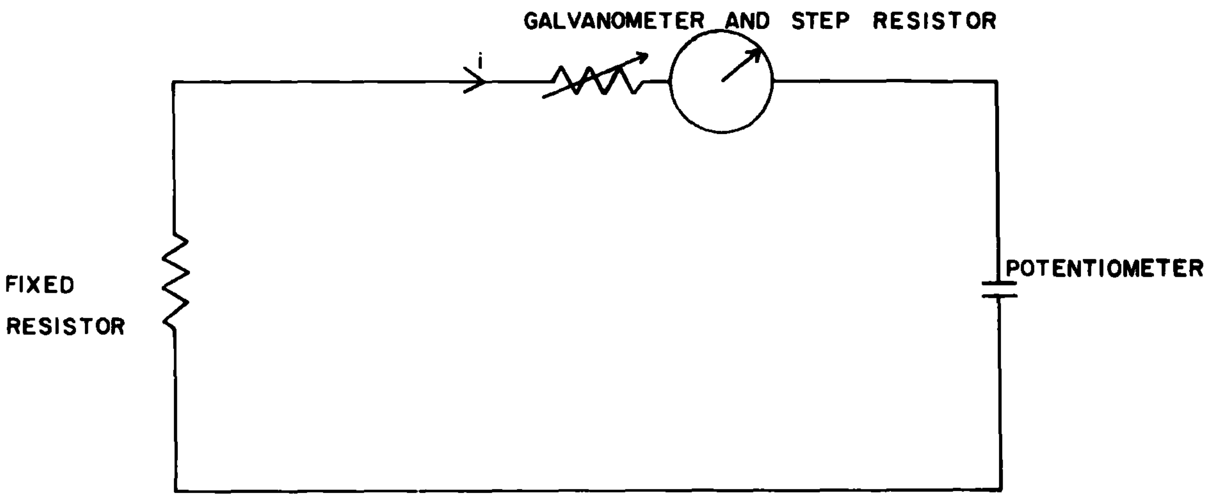

FIGURE 2 FOR DETERMINING THE LINEARITY OF GALVANOMETER ON THE 1, 1/10, AND 1/100th SCALES

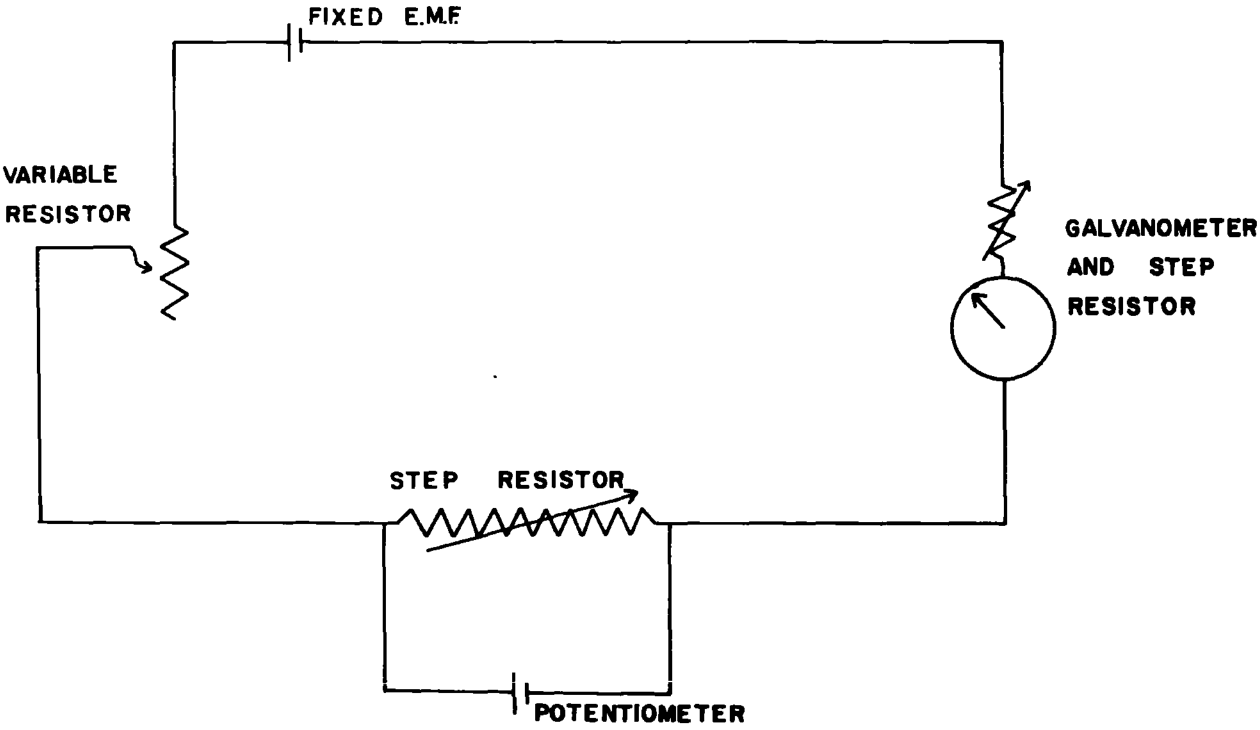

FIGURE 3 LINEARITY OF THE 1/100th AND 1/1000th SCALES

Part 2: The relationship between the 1/10th and the 1, 1/100th and 1/1000th scales

To determine the scale relationship between the 1/10th and the 1 and 1/100th scales the same circuit was used as in Part I.

The results obtained were:-

Scale	Voltage	Divisions	Divisions/Volts	Difference
	V	D	D/V	
	volts	divisions	divisions/volt	percent
1	1.35	9.41	6.97	0.2
1	0.0	0.00		
1/10	0.0	0.00	6.96	
1/10	10.80	7.51		
1/10	1.35	6.53	4.83	0.25
1/10	0.0	0.00		
1/100	10.80	5.21	4.82	
1/100	0.0	0.00		

The circuit used for the 1, 1/10th and 1/100th scales was not flexible enough to include measurements on the 1/1000th scale so a different circuit (figure 3, appendix I), was constructed. This circuit used a variable wire resistor (uncalibrated) and a calibrated step resistor that had a full range of 1 to 9999 ohms, a battery of fixed E.M.F. and the galvanometer were also put into the circuit. The apparatus was connected and the step resistor altered until 100 scale divisions were given on the galvanometer, then a potentiometer with a maximum E.M.F. of 2.5 volts and reading ± 0.0001 of a volt was connected across the step resistor and the voltage read and recorded. The ratio of the voltage to the resistance gives the current for 100 scale divisions; and the values calculated for the 1/100th and 1/1000th scales compared.

The results obtained were:-

Scale	Divisions D divisions	Voltage V volts	Resistance R ohms	Current i amps	Difference percent
1/1000	0	0	0	0	
1/1000	100	0.7543	738	0.001011	1.0
1/100	100	0.9775	9553	0.001021 ÷ 10	

Conclusion; the times 1, 1/10th and 1/100th scales differ by less than ½% while the times 1/100th and 1/1000th scales differ by 1%. Because of the close agreement between the different scales, it is assumed that they are all linear to the same degree as the times 1/10 scale, that is ± 1.5%.

Appendix II

The computer programme for calculating reflectivity in air. The equations on which this programme is based are given at the end of the section on "Calculation of the Intensity of the different light rays".

```
REFLECTIVITY IN AIR
BEGIN ARRAY T(1:20)
     REAL IO,ID5,ID6,ID7,I5,I6,X,Y,Z,W,P,RO,R,TH,AD,BB,DD,S'
     INTEGER M'
     SWITCH SS:=LL1'

LL1:M:=1'  READ INSTRING(T,M)'  M:=1'  PRINT OUTSTRING(T,M)'
READ IO,ID5,ID6,ID7,I5,I6'
X:=ID5/ID6'  Y:=ID7/ID6'  Z:=(Y** 2-1)/(Y **2-1)'
W:=Y+X* (SQRT(Z))'
P:=(ID7/IO) *(((W ** 2-1-Z) ** 2-4* Z)/(W** 2 *(SQRT(Z))* (W ** 2+1-Z)))'
RO:=1/W + P/2 + (SQRT(R **2/4+ P/W))'
R:=1/(W *RO)'
TH:= RO *(SQRT(Z))'
AD:=(R/TH)* ((1-R)** 2 *(TH** 2-RO** 2)-(1-R ** 2 *RO ** 2+R** 2 *TH** 2))
     /((1-R) ** 2-2 *R ** 2)'
BD:= (1-R **2* RO **2+ R **2* TH **2)/(TH *((1-R) **2-2 * R **2))'
DD:= 2* R/((1-R) **2-2 * R **2)'
S:=(BD-DD *I5/I6)/(I5/I6)/)I5/I6-AD)'
PRINT ££L2??,ALIGNED(2,8),RO,R,TH,S,££L6??'
GOTO LL1'
END'
```

To run the programme read in the 5 hole Algol library tape under 40 0; when the "Algol ready" message is given, read in the programme by changing the sign digit. The programme is read in, and immediately the title "Reflectivity in air" is printed out; there is a 30 second pause while the programme is compiled followed by a "free store" message and a "data wait", the data is read in by changing the leftmost F2 digit, and the results are printed out, either on paper tape or directly by the teleprinter as desired.

The programme takes about 3 minutes to read in and another 30 seconds to compile, and each set of data takes approximately 15 seconds to read in, 4 seconds to calculate and 30 seconds to punch out on paper tape. As many sets of data as desired can be run at one time; so once the programme has been read in and compiled, a set of data can be calculated and punched out approximately once every minute.

Facility is provided in the programme for a title, which must be enclosed by a £ and ? sign, and will be printed out at the head of each set of results. The data must be read in, in the same order as shown in the "read" statement of the programme.

The data given in table 5 would be read in as:-

```
£April 22/65 NO.1?

8.99  1.04  0.0383  2.73  1.02  0.166
```

This will then be printed out as:-

```
April 22/65 NO.1

0.12920534

0.05427498

0.33936083

0.40685520
```

Where the numbers correspond to θ, r, e and S respectively.

Appendix III

The computer programme for calculating reflectivity in oil. The equations on which this programme is based are given at the end of the section on "Calculation of the Intensity of the different light rays".

```
REFLECTIVITY IN OIL, USING KNOWN VALUE FOR REFLECTIVITY OF GLASS IN OIL'

BEGIN ARRAY T(1;20)'
     REAL IO,ID5,ID6,ID7,I5,I6,WW,X,Y,Z,W,P,RO,TH,AD,BD,DD,S,R'
     INTEGER M'
     SWITCH SS:=LL1'

LL1:M:=1'  READ INSTRING(T,M)'  M:=1'  PRINT OUTSTRING(T,M)'
READ IO,ID5,ID6,ID7,I5,I6,WW'
X:=ID5/ID6'  Y:=ID7/ID6'  Z:=(Y** 2-1)/(X** 2-1)'
W:=Y+X *(SQRT(Z))'
P:=ID7/IO *(((1-(1/W ** 2)-(Z/W **2) ** 2)-(4* Z/W **4))/
    ((1+(1/W ** 2)-(Z/W **2)) * SQRT(Z)))'
RO:=1/W+P/2+SQRT((P **2/4)+P/W)'
TH:=RO *SQRT(Z)'
R:=1/(W *RO)'
AD:=((R *(1-WW)** 2 * (TH** 2-RO** 2))-(WW* (1-(R* WW *RO** 2)+(RO* WW *TH**2))))/
     (TH *(((1-WW)** 2)-(WW *(R+WW))))'
BD:=(1-(R * WW *RO ** 2)+(R * WW *TH ** 2))/(TH *(((1-WW)** 2)-(WW *(R+WW))))'
DD:=(R+WW)/(((1-WW) **2)-(WW *(R+WW)))'
S:=(BD-(I5/I6 *DD))/(I5/I6-AD)'
PRINT ££L2??, ALIGNED(2,8),RO,TH,R,S,££L6??
GOTO LL1'
END'
```

This programme is read in, in exactly the same way as the one for reflectivity in air, and takes approximately the same time. The only difference is that, the reflection coefficient of the glass in oil must be included as the last figure in the data tape, i.e., after 0.166 in the previous example.

Appendix IV

The computer programme for the least squares solution of the equation $\overline{V} = a + b\sin\theta\cos\theta + c\sin^2\theta$.

```
LSTSQ (CURVE)'
BEGIN ARRAY AA(1:3,1:3), BB, CC, FF(1:3,1:1), DD(1:60,1:3), EE(1:3,1:60),
     V, THETA(1:60)'
     REAL VSQUARE, COST, SINT, RMS, R, RMSV, RMSA, RMSB, VO, PE'
     INTEGER I,J,N'
     SWITCH SS:=START'

N:=1'  INSTRING(V,N)'  N:=1'  OUTSTRING(V,N)'
FOR I:=1 STEP 1 UNTIL 60 DO BEGIN
FOR J:=1 STEP 1 UNTIL 3 DO
DD(I,J):=0'
END'

CC(1,1):= CC(2,1):= CC(3,1):= 0'
I:=0'
VSQUARE :=0'
START:I:=I+1'
READ V(I), THETA(I)'
IF V(I) NOTEQ 0 THEN BEGIN
THETA(I):=THETA(I) * 0.01745327'
SINT:=SIN(THETA(I))'
COST:=COS(THETA(I))'
DD(I,1):=1'
DD(I,2):=SINT *COST'
DD(I,3):=SINT **2'
CC(1,1):=CC(1,1)+ V(I)'
CC(2,1):=CC(2,1)+(V(I)* SINT *COST)'
CC(3,1):=CC(3,1)+(V(I)* SINT **2)'
VSQUARE:= VSQUARE+(V(I)** 2)'

GOTO START'
END'
```

```
I:=I-1'
MXCOPY(FF,CC)'
MXTRANS(EE,DD)'
MXPROD(AA,EE,DD)'
INVMX(AA)'
MXPROD(BB,AA,CC)'

PRINTMX(BB)'
RMS:= SQRT(ABS(VSQUARE-BB(1,1)* FF(1,1)-BB(2,1)* FF(2,1)-BB(3,1)* FF(3,1))/
      (I-3))'
RMSV:=SQRT(AA(1,1)) *RMS'
RMSA:=SQRT(AA(2,2)) *RMS'
RMSB:=SQRT(AA(3,3)) *RMS'
PRINT ££L2?RMS:=?,SAMELINE,RMS'
PRINT ££L2?RMSA:= ?,SAMELINE,RMSV'
PRINT ££L2?RMSB:= ?,SAMELINE,RMSA'
PRINT ££L2RMSC:= ?,SAMELINE,RMSB'
FOR N:=1 STEP 1 UNTIL I DO BEGIN
R:=V(N)-BB(1,1)-BB(2,1)* DD(N,2)-BB(3,1)* DD(N,3)'
PE:=(R/V(N)) *100'
PRINT  ££L??, ALIGNED(4,7),V(N),SAMELINE,THETA(N),R,PE'
END'
END'
END'
END'
```

To run this programme read in the 5 hole Algol library tape under 40 0, when the "Algol ready" message is given, read in the library matrix package tape number 803 M114, also under 40 0, immediately following, read in the programme by changing the sign digit. The programme takes $3\frac{3}{4}$ minutes to read in, the title "matrix package, lstsq (curve)" is printed out, there is a $4\frac{1}{4}$ minute wait while the programme is compiled, after which the "free store" message is given and a "data wait" occurs. The data is read in, in approximately $\frac{1}{4}$ minute and it takes another $\frac{3}{4}$ of a minute to be calculated and the data to be punched out on paper tape.

Facility is provided for a title; the data must be read in with voltage first and angle second, and data will continue to be read in until a voltage of 0 appears , when all the data preceding this stage will be calculated and the results punched out. A typical set of data would be:-

```
£April 11/65, wavelength=589nm?

0.538  10.0
2.020  20.0
4.261  30.0
6.92  40.0
9.14  50.0
0.00  00.0
```

A maximum of 60 pairs of data can be calculated at one time.

The print out of this data would be:-

```
April 11/65, wavelength = 589nm

-.053
 .586
16.194
RMS = .011
RMSA=  .023
RMSB=  .093
RMSC= -.057
```

```
0.538  0.175  0.003  0.526
2.020  0.349 -0.009 -0.467
4.261  0.524  0.012  0.278
6.920  0.698 -0.007 -0.095
9.140  0.873  0.001  0.013
0.000
```

Where the 3 single numbers at the top are a, b, and c respectively, RMS is the standard deviation of $\bar{\bar{v}}$, and the others labelled. The 4 columns are, from left to right, the voltage, the angle (in radians), the residual and the percentage residual. All values are, in actual fact, printed out to 7 decimal places.

PART 2

THE DISTRIBUTION OF HEAVY METALS IN GRANITES

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Chapter 1

Introduction

As the search for economic mineralisation continues, those deposits which are easily located by a simple examination of the earth's surface have in large part been located, and new methods of exploration for finding "blind orebodies" with no visual surface indication have been developed. One such exploration technique, which has only been used extensively since the war, is based on the detection of secondary geochemical dispersion patterns and has proved itself in many instances (see Hawkes and Webb, 1962, for examples and case histories). The use of primary geochemical dispersion is not so well developed and in the words of Hawkes and Webb, "the application of primary dispersion patterns to mineral exploration is still strictly in the experimental stage". The British Isles, containing both the mineralised (and well explored) granites of Devon and Cornwall, and non-mineralised granites, seemed to be an ideal location to test the extent to which primary dispersion may be useful in exploration. The aim of the present study was not to locate new areas of possible economic mineralisation but to collect further basic data concerning such variables as the levels of trace element concentration in mineralised and non-mineralised granites; the variation of trace elements away from mineralisation; and the ratio of major to trace elements in both types of granite. It is hoped to add to the already available data, information which will make a significant contribution to the use of primary dispersion patterns in unexplored areas. A short review of the available information pertinent to this subject is given, but for a full discussion of the theory and uses of all phases of applied geochemistry the reader is referred to the excellent book by Hawkes and Webb.

Previous Work

Following the classification of Hawkes and Webb (op. cit., table 1) the primary dispersion patterns are divided into two types, syngenetic and epigenetic, each with further sub-divisions. The patterns of interest during this present study are the two syngenetic patterns

Table 1

Classification of the Principal Types of Primary Dispersion Patterns (after Hawkes and Webb, 1962, p.46).

Syngenetic Patterns		Geochemical province
		Local syngenetic patterns
Epigenetic Patterns	Hydrothermal dispersion patterns	Wall-rock anomalies
		Leakage anomalies
		Compositional zoning
	Pressure Temperature effects in epigenetic minerals	Mineral reconstitution
		Chemical geothermometers
		Isotopic geothermometers

(geochemical province and local syngenetic pattern) and the hydrothermal dispersion patterns of the epigenetic types.

Syngenetic patterns

A geochemical province may be defined as a relatively large segment of the earth's crust in which one or more elements are in greater abundance than its "Clark", or average, for the earth's crust. The geochemical province should, if it is a true geochemical province, cover more than one age and one rock type. If the element or elements in question are of economic importance it does not necessarily follow that concentration of ore grade will exist, because, although the element will be in greater abundance than normal, it may be too disseminated to form an economic or even sub-economic deposit.

A metallogenetic province was defined by Bateman (1959) as a "certain region characterised by relatively abundant mineralisation, dominantly of one type", e.g. the copper mineralisation of Arizona, gold mineralisation of the Canadian shield etc. This differs from a geochemical province in that the mineralisation may be the result of any process of concentration of elements initially present only in average amounts (i.e. about the Clark), brought about by some condition of tectonism etc., or the effect of an unusual abundance of an economically important mineral. In the latter case the metallogenetic and the geochemical provinces coincide. Turneaure (1955), gives a complete review of the metallogenetic provinces using as examples the copper-producing area of Peru and Chile, the tin fields of north-west Europe, uranium fields of the Canadian shield and many others. This concept, however, is rather vague as to its limits, and frequently there is difficulty in deciding whether or not a particular area constitutes a geochemical (or metallogenetic) province.

It is when the metallogenetic and geochemical provinces coincide, as frequently seems to be the case, that geochemical exploration can be most useful in determining the most likely area of mineralisation. Instances have been reported however, when the geochemical and metallogenetic province do not coincide. Discussion and examples of both cases are given shortly.

If the area in which the concentration of a particular element is high, is measured in miles rather than in hundreds of miles, it is generally considered that the origin of the anomalously high area can more readily be ascribed to local processes of petrogenesis, differentiation or metamorphism etc., rather than to a similar condition over a much larger area or a primeval difference in the composition of the earth's crust. For this reason the local areas of high trace metal content are termed local syngenetic patterns, rather than geochemical provinces. It will be evident that this division between geochemical province and local syngenetic pattern is rather arbitrary and for this reason no attempt is made here to assign the patterns found during the present study to one type or the other, rather they are referred to collectively as syngenetic patterns.

Ingerson (1954) re-stated an old problem, when he summarised in theoretical discussion the possibility of using trace element concentrations in igneous and adjacent rocks for mineral exploration. He concluded that; either the intrusion with associated economic mineralisation had a high trace metal content, (i.e. the intrusion was originally abnormally high in the economic minerals or well above the "Clark", in which case the geochemical and metallogenetic provinces coincide); or, the intrusion had only an average content of economic minerals (i.e. all these minerals became concentrated into a deposit, and so the concentration of the pertinent minerals in the country rock is very low in which case the geochemical and metallogenetic provinces do not coincide). Reviewing the literature, instances of either case can be found Mackin (1947) for example, working at Iron Springs, Utah, analysed the quartz monzonite adjacent to magnetite mineralisation and found that it was very low in iron, whereas the quartz monzonite on the edge of the intrusion had close to an average content. Working in Utah and Nevada, but concerning themselves with the copper-lead-zinc mineralisation, Parry and Nackowski (1963), analysed the biotite from twelve different stocks for copper, lead and zinc. While they found a positive correlation between copper concentration in the biotite and copper mineralisation, they found an inverse correlation for lead and zinc, i.e., high lead and zinc concentrations in the biotites from non-mineralised areas, and vice-versa. Phair (1952), found that uranium-bearing bostonites in Colarado were lower in uranium close to the uranium-bearing veins than the bostonites further away. Discussing the origin of mineralisation on the flanks of an intrusion Larson (1928, p.432) concludes, "magmas commonly give rise to contact metamorphic zones composed of constituents in which they are low. For instance, granite and granodiorite low in magnesium and iron form large contact deposits which are rich in magnesium and iron".

If low trace element concentration is associated with economic mineralisation, the converse might also be expected, i.e. high trace element concentration associated with no deposits of economic minerals. Although such "negative results" are not often reported in the literature, several examples do exist as in the determination of the trace element content of the basic rocks of the Skaergaard intrusion by Wager and Mitchell (1951). They found an average copper concentration for the original magma of 150ppm. The intrusion has no known associated copper mineralisation and this value is about twice as high as the average given by Vinogradov (1956), who reports an average of 80ppm copper for basic rocks (taken from 8 mainly Russian papers). Green (1959) found the same result when summarising all available analyses. Sandell and Goldich (1943), in analysing gabbro and greenstone from Minnesota, which have no known copper mineralisation also report an average value of 150ppm copper, again about twice as high as for other areas. Oftedal (1939) discovered an average tin content for Norwegian rocks of 0.1% (the average for the lithosphere is 0.004% as reported by Goldschmidt, 1954) which makes it a tin rich area, while Norway has no known tin deposits and is generally known as a country with a tin defficiency. Several other examples of this type also exist although they are not common.

There also appears in the literature numerous examples of high trace metal content in the country rock associated with economic mineralisation. For example, Goldschmidt (1954, p.393), working on tin found high trace concentrations of tin in granites associated with mineral deposits and low tin concentrations if no mineralisation were present. Goloubinoff (1927), Ahrens and Leibenberg (1950) and Itiskson (1963), also report high tin values for rocks related to tin mineralisation. Warren and Delavault (1960), found after testing 10 intrusions in British Columbia, that of the 7 with no associated mineralisation none averaged higher than 5ppm copper, while the 3 intrusions with known associated mineralisation averaged 52, 43 and 31ppm of copper. Gross (1952) discovered an association of radioactive minerals in silica with gold mineralisation in granite stocks at Red Lake, Ontario. Also in Ontario, Slawson and Nackowski (1959) found a correlation between anomalously high lead concentration in quartz monzonites in lead mining areas as compared with lower lead values in non-mineralised stocks. In France, Jedwab (1955), found the average tin concentration in micas from mineralised areas to be about twice as high as the tin content in micas from a non-productive area.

Whilst the successful use of this type of syngenetic pattern has given encouragement to the use of this criterion in the field, care must be taken not to apply this principle universally, as such variations can arise solely as the result of progressive fractionation of the host rock. This point was well demonstrated by Heier and Taylor (1959) who, when working on two adjacent non-mineralised Pre-Cambrian granites found the average content of the lead in the alkali feldspars to be 9ppm for one stock and 26ppm for the other. They concluded that the difference was entirely due to the degree of fractionation. Rogers (1958), in a study of the White Tank quartz monzonite California, came to the conclusion that the barium, lead and strontium concentrations in K-feldspar decreased from the older to the younger rocks. Sen, Nockolds and Allen (1959), also working on igneous rocks in California came to the same conclusion as Rogers, and similar results have been reported by other authors. So, while in a limited number of cases this type of syngenetic pattern has proved itself very useful, caution is required in interpreting the results, and in particular if the host rock has undergone any fractionation this should be determined if possible.

It appears from the literature that two types of areas may be found, firstly those with a high trace metal concentration associated with economic mineralisation, and a low trace metal concentration associated with barren zones and secondly: those with a low trace metal concentration associated with economic mineralisation, and high trace metal concentration associated with barren zones. While these fundamental differences are found between areas, it appears that in any one area both the above conditions will not be encountered and, in fact, a fairly uniform trace element content is found. For example, Putman and Burnham (1963) did 3 parallel traverses of about 150 miles each, crossing plutons, dykes and 7 major intrusions, and came to the conclusion that, "the minor element content in the ferromagnesians for any one pluton is fairly uniform, ... a significant difference exists from pluton to pluton ... and the differences displayed by trace elements between certain like rocks, may be as great as between diorite and granite". Although several other workers have found two distinct trace element populations for one pluton with two phases, they conclude that much the same principles apply, (e.g. Slawson and Nackowski, 1959). Bray (1942) after analysing the total rock and five individual minerals for a total of 19 elements, went further when he came to the conclusion that, "from quantitative analyses of rocks, a scheme may be set up whereby any rock in the district can be identified on the basis of its minor element content. Although fundamental differences can be found from area to area, it appears that any one area can be treated as essentially homogeneous, (this problem is discussed further when considering sampling density).

The most obvious conclusion to come to is that, either case 1 or case 2 may exist, and before an exploration survey is conducted in any area an "orientation survey" should be carried out near known mineralisation. This will determine whether high or low trace element concentration is associated with economic mineralisation in that particular area. Hawkes and Webb (1962, p.27), state that, "significant anomalies are characterised by abnormally high concentrations of indicator elements; 'negative' anomalies, or patterns of abnormally low values, rarely have any application in exploration", and they recommend the use of the orientation survey.

Epigenetic Patterns

Hydrothermal dispersion patterns

Here, the term "hydrothermal" is used in its broadest sense to indicate hot aqueous fluids, whatever their source or direction of movement, transporting the economic minerals. This introduction of ore minerals may be by diffusion through a liquid or gas saturated rock, or a mass movement of the fluid itself. During the present study there was the opportunity to examine and analyse wall-rock adjacent to mineralisation but none of the other epigenetic patterns mentioned by Hawkes and Webb (1962). Therefore only wall-rock anomalies are considered further.

Wall-rock anomalies

As the ore is emplaced, the wall rocks surrounding the deposit also tends to be slightly enriched by the ore forming solution. This may have the result of forming a local "high" or aureole of the ore mineral in the wall-rock which if detected effectively extends the useful "ore" zone and increases the chances of discovery.

Wall-rock anomalies have been successfully used in the past by several workers:- e.g. Morris and Lovering (1952), working in the Tintic district of Utah, concluding that diffusion was mainly responsible for the movement of the ore into the wall-rock, were able to predict accurately the location of a blind ore body. They found that the metal content of the wall-rock fell off logarithmically from the ore deposit, except where cracks permitted greater travel than normal. Along these cracks the metal content generally was found to fall off linearly from the deposit. The width of the anomaly seemed to vary with the chemical reactivity of the wall-rock. In limestone the transportation distance was found to be very low, sometimes being restricted to as little as five feet. This very short aureole has been reported by others as characteristic of limestone; e.g., Engel and Engel (1956) and Austin and Nackowski (1958). In a less reactive environment, e.g. metamorphic silicate rocks and igneous rocks, Morris and Lovering reported aureoles up to thousands of feet wide. James (as reported in Hawkes and Webb, 1962), in his study of the arsenic in the wall-rock of the shear zones containing arsenic and gold in southern Rhodesia, discovered a logarithmic decay of the arsenic content away from the ore deposit. He records an aureole width of 25 feet for sandstones and 200 feet for greenstone. Stoll (1945) working on the beryllium pegmatite of New England found diffusion of the beryllium from the pegmatite into the mica-schist and mica-gneiss country rock. Although his work did not establish the exact shape of the aureole, anomalously high concentrations of beryllium were found several hundred feet from the pegmatite veins. Considering the variable width of wall-rock anomalies Hawkes and Webb concluded that, "either the chemical activity or the permeability of the rock types, together with the duration of the period of hydrothermal activity", is responsible for the large difference in aureole width.

Faults, joints and fractures are other variables which may cause confusing anomalies in wall-rocks. Graf and Kerr (1950), during a geochemical survey around lead-zinc deposits in a limestone formation, New Mexico, found that the lead highs were further from the body than the zinc highs. This is the reverse of what might be expected, as zinc is the most mobile element. They found also that the zinc concentration was variable, not showing any direct correlation with distance from the ore deposit. They concluded that the element distribution was largely controlled by small fractures.

The pattern of wall-rock anomalies can, of course, be confused or even completely masked by supergene leaching, and in some cases a completely unusable pattern may emerge. However, the instances of usable wall-rock anomalies are encouragingly high.

Total Rock versus Mineral Surveys

It has been clearly demonstrated in the past that elements occurring in trace amounts tend to concentrate in certain minerals, as determined by their charge, ionic radius and other physical properties (Goldschmidt, 1954; Wager and Mitchell 1943 and 1951, and others). Because of this effect, if total rock is analysed, quite large differences in the recorded level of concentration could be caused simply by the change in the mode of the rock. For example, nickel is known to occur almost entirely in the ferromagnesian phase and if the mode of this phase doubles an apparently significant change in the nickel concentration will result.

In order to remove this effect, it seems desirable, at least for an initial study, to analyse individual minerals rather than total rock. Several workers in the past have, with success, undertaken such studies, e.g. Slawson and Nackowski (1959), worked on lead in K-feldspars; Bush and Cook (1960), analysed jasperoid for heavy metals; Putman and Burnham (1963), copper in biotite; Jedwab (1955), tin content in several minerals; etc. The majority of workers, particularly for earlier analyses, have used total rock surveys and so the need for more analyses of individual minerals is apparent. While it is difficult to give any exact figures, it does appear from work already published that mineral surveys have a higher incidence of success than total rock surveys.

Rock weathering

Yet another effect which may mask the true primary dispersion pattern is the alteration of the trace element content due to rock weathering. While the exact magnitude of this effect has not been reported in the literature, it seems quite possible that the movement of surface and near surface water, particularly with the associated oxidising conditions, may partially or completely distort or conceal the original pattern. While the lack of fresh (i.e. unweathered) exposure may make it necessary to use weathered rocks, as far as possible, in order to gain maximum control and to reduce the number of variables to a minimum, it is desirable to analyse unweathered rock.

Conclusions

It appears from the literature that while certain studies into primary dispersion patterns have been undertaken, there is still a need for detailed studies from a large variety of different areas, the instances of mineral rather than total rock surveys particularly on unweathered samples being rather few. The British Isles seemed an ideal location to carry out further studies into this problem particularly with their extensive areas of mineralised and non-mineralised granites, both of which have been well mapped and explored. In addition, the British granites are better traversed with roads, quarries and other fresh exposures than most areas in the world, thus allowing the collection of a reasonable number of fresh samples from most parts of any granite body. Considering the distribution of the British granites and the complete lack of similar work published for them, the possibility of a study of the syngenetic patterns over a large area and also the wall-rock anomalies from specific mines seemed ideal. In addition to the possibility of determining some method for distinguishing mineralised from non-mineralised granites and the use of wall-rock alteration for further exploration such a study could be expected to give information regarding the variation of a trace element population within a granite and also different phases of the same granite, and give some indication of the number and distribution of samples which should be collected during exploration in an unexplored area.

Chapter 2

Collection, Separation and Analysis of Samples

Areas Examined

The present study was confined to the granites of Great Britain, and specifically to the Hercynian granites of Devon and Cornwall and certain Caledonian granites of Scotland. In the time available it was impossible to sample adequately all British granites and so these two regions were chosen to give roughly equal areas of mineralised and non-mineralised granite and also to satisfy as far as possible the sample patterns discussed below. Diagram 1 is an outline map showing the location of the granites in Great Britain, with those examined in the present study indicated.

Samples were taken from all the major stocks in Devon and Cornwall and a total of 60 specimens were analysed. For comparison with these samples from mineralised granites 104 specimens were analysed from 8 different granite stocks of Caledonian age including the Shap and Weardale granites in Northern England and 6 stocks in Scotland.

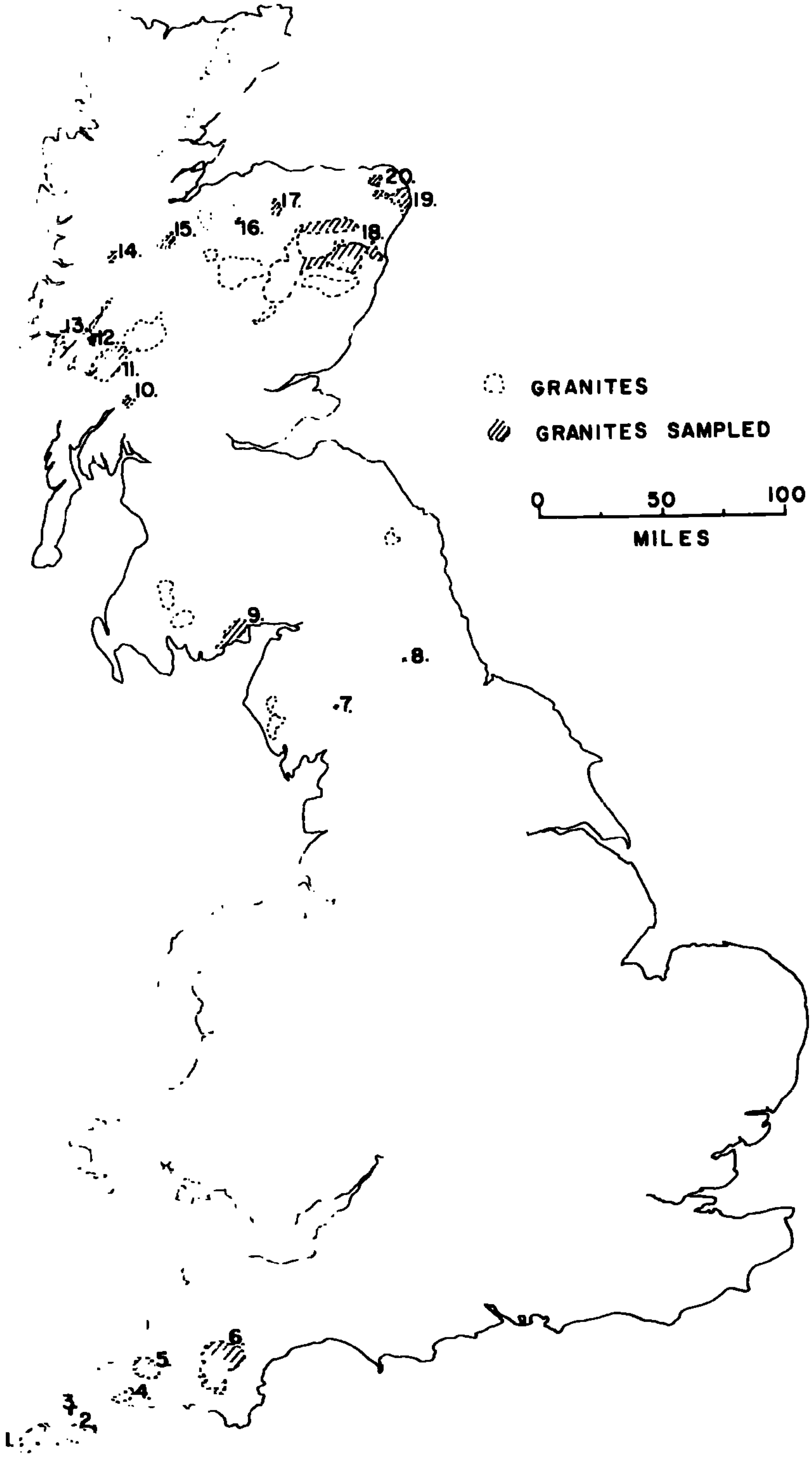
Sampling Method

In the introduction it was pointed out that it is desirable to remove the variable and possible error due to rock weathering as much as possible. In order to do this, after choosing suitable mineralised and non-mineralised granites, sample locations within these areas were selected to give fresh samples, i.e. quarries, mines, dam sites and similar excavations which in general were post-war and preferably still in use. Although such samples were not common, where they showed mineralisation on joint faces etc., they were discarded and others taken. By using this sampling method, which is not truly random, it is possible that a bias may be introduced into the results, particularly as the result of an unequal sample distribution. However, as each phase of each stock was treated separately for a detailed interpretation of the results any error due to taking different numbers of samples from different areas was avoided. In order to reduce any further bias, as wide a distribution as possible

Diagram 1

Outline Map of Great Britain showing Granites sampled

1. Lands End
2. Carnmenellis
3. Cligga Head
4. St. Austell
5. Bodmin Moor
6. Dartmoor
7. Shap
8. Weardale (Rookhope borehole)
9. Criffell-Dalbeattie
10. Allt na Lairige
11. Etive Complex
12. Ballachulish
13. Strontian
14. Cluanie
15. Foyers
16. Granton
17. Dufftown
18. Aberdeen Area
19. Peterhead
20. Fraserburgh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1

DIAGRAM I

over any one granite stock was obtained, and in particular samples were generally taken at least one mile apart. Whether or not the number of samples taken from each individual phase was sufficient will be discussed next.

In the present study a sampling density which would establish any significant difference between two stocks or phases is desired, but to find the significant difference depends on:- 1. the level of difference, whether two populations differ by 10, 100 or 1000% etc., and 2. the variation of results (due to both natural variations and analytical errors) in each population. In practice the actual level of significant difference which can be detected will be controlled by the number of samples taken and the variability within each stock. It is therefore, desirable to estimate the variability and see what sampling density is required before the desired significant difference can be detected.

It appears from the literature that some granites show considerably more variability than others even when both (or all) have been sampled and analysed by the same person (subsequent analyses included in this thesis will bear this out). An estimate of the variation of any one granite is clearly impossible without at least several analyses, and as sufficient were not available for the different British granites, the data from other areas had to be relied on. When choosing the level of significance desired, the practical aspect of available facilities for analysis, the time taken for one sample (in this case, crushing, separating, and analysis took about 5 to 6 hours), and the fact that only if the number of samples is squared will the level of significant difference detected be halved, must be considered. Putman and Burnham (1963) found the significant difference at the 95% level for an average of 11 samples per stock, to be 0.15 of the log means for nickel, cobalt, vanadium, chromium and sometimes zinc, and 0.20 for lead, copper and sometimes zinc. This means that at the 100ppm level the means must differ by about 40% in the former case, and 60% in the latter, to be of significance, with slight decreases in the difference required as the concentration increases. Putman and Burnham based their figures on the t-test analysis,and concluded that about 10 samples per stock was a practical number. Slawson and Nackowski (1959) did not apply any statistical test but also concluded that 10 samples was a practical number.

In the present study 10 samples were taken wherever possible from each stock, and, in some cases more were easily obtained and in other cases less, the average being 9 samples for 13 stocks. Considering the work of Putman and Burnham it seemed unlikely that if two means (for trace elements only) differed by less than 40% that this would represent any significant difference, while a difference greater than 60% would generally be significant. Because of the greater uniformity of the major elements much smaller differences in the mean should be significant. While the t-test used by Putman and Burnham should normally be quite adequate it does make the assumption that the populations being tested show normal distribution. In preference to the t-test non-parametric statistics were used in the present study, and in particular the Wilcoxon two-sample test for the unpaired case (see Alder and Roessler 1964, for a complete discussion on the uses and applications of this test). A probability level of 95% or higher was taken as significant. To test the present analyses, determinations were made by the Wilcoxon test on the level of the probability of a significant difference between two means established during the present study. The results are shown in table 2 from which it can be seen that the trace figures agree quite well with those of Putman and Burnham, i.e., generally speaking a difference in means of greater than 50% is significant. For the major elements a difference in means of about 10% was found to be significant. If there is any doubt about the significance of the difference between two means discussed in the body of the text the Wilcoxon test is applied to them.

Where a significant difference was found to exist using the present sampling procedure, a further test using a truly random sampling pattern and weathered rock could then be carried out to test these variables, but time was not available for any such analyses.

Minerals Analysed

As well as removing the unknown factors due to rock weathering the present study was designed to eliminate variations due to changes in the modal composition of the rock. In order to do this three fractions were

Table 2

The Probability of Significant Difference Between Two Means as Established by the Wilcoxon Test

Comparison between samples from mineralised and non-mineralised granites

Element	Sample	% Difference in Means	% Probability
Cu	feldspar	8	53
Zn	biotite	18	60
Cu	biotite	20	81
Pb	feldspar	56	97.3
Pb	biotite	84	100
Zn	feldspar	275	100

Comparison between samples from the Cornish plus Weardale granites and the Scottish granites

Element	Sample	% Difference in Means	% Probability
Na	feldspar	14	96.3
K	biotite	29	99.5
K	feldspar	66	100
Ca	feldspar	157	100

analysed independently - the leucocratic fraction (consisting of the feldspars and quartz), pure biotite, and pure muscovite, (the latter two only if sufficient could be separated).

Sample Preparation

The samples were first split into approximately one inch pieces using a hydraulic press and then crushed to about 1/8 of an inch using a piston and plunger arrangement on the same press. This material was then transferred to a tungsten carbide vial and ground, using a Spex mixer mill so that the material would pass through a 50 mesh sieve. The resultant powder was washed with water in a 150 mesh sieve until a perfectly dust free powder between 50 and 150 mesh remained. In order to have enough biotite or muscovite for subsequent analysis between 25 and 50 grammes of powder was obtained from each sample, depending on the initial concentration of the biotite and muscovite.

The washed powder was dried at 105° C and the magnetite removed using a hand magnet. The remainder of the sample was passed through a Cook magnetic separator which was sufficient to separate all the ferromagnesian minerals with about 98% purity; the biotite was then separated from any other associated ferromagnesian minerals by "panning" with a large sheet of paper (where the rounded horneblende, sphene and any feldspar etc., rolls to the bottom, and biotite stays near the top of the paper leaving a powder of at least 98% purity). Muscovite is easily separated from feldspar and quartz, first using the magnetic separator and finally the same system of "panning", the final powder being approximately 98% pure. The feldspar plus quartz fraction is easily upgraded to 99% purity by further magnetic separation. As there is considerably more feldspar and quartz than required a fair proportion can be wasted in gaining purity.

In an attempt to separate the feldspar from the quartz so that pure feldspar could be analysed the techniques outlined below were attempted. The normal method of separation using heavy liquids was tried first, but as the oligoclase in particular (specific gravity 2.650) was very difficult to separate from quartz (specific gravity 2.656) a graded density column of the type developed by the Warren Spring Laboratory (L.D. Muller, personal communication) was tried. After setting up a suitable graded density column in a coaxial tube and centrifuging, a good separation of the two feldspars and quartz was obtained, but unfortunately a maximum of only one gramme could be separated at one time, leaving approximately one third of a gramme of each fraction. The time taken to get the three grammes required for x-ray fluorescence plus the half gramme for wet chemical analysis took too long to make this technique feasible. As an alternative, a method using froth flotation as developed by British Industrial Sand (H.D. Segrove, personal communication) was attempted, but a purity of greater than 90% was very difficult to attain and also this method required the use of dilute hydrofluoric acid which might well etch the minerals and remove some of the trace elements. All the techniques tried were either too lengthy or did not produce fractions of sufficient purity, and as it is hoped that this method will have some application to geochemical prospecting it is desirable to keep it as rapid and simple as possible. For the final interpretation, an estimate of the quartz content was made using x-ray diffraction as described later.

The separate fractions were finally ground for a further half hour in the mixer mill so that there was no "gritty" feel to the final powder which was estimated to be about 300 mesh.

Element Analysis

Of main interest to this study are the heavy metals, namely lead, copper, zinc, nickel, tin and iron. In addition several major elements may be of use in interpreting the trace metal results, e.g. calcium, sodium, potassium, strontium and zirconium, give an indication of the composition of the granite and in particular the degree of fractionation if any. Such elements as potassium may "control" the number of crystal lattice sites available for lead, and therefore a change in the lead concentration may simply reflect a change in the potassium concentration. The effect of such a variable could easily be determined if the potassium concentration is known.

The facilities available for quantitative analysis included x-ray fluorescence and a wet chemical laboratory. The x-ray was used to determine all trace elements above the detectibility limit, namely lead, zinc, copper, nickel, strontium, rubidium, zirconium, chromium and manganese; unfortunately tin could not be determined because of interference of a tungsten line from the tungsten target of the x-ray tube. Iron was found to be too variable to be of any practical use and therefore time was not taken to analyse for this element. In addition the x-ray fluorescence was used to analyse for calcium. Sodium and potassium were determined relatively rapidly using the flame photometer but further analysis for major elements was judged to take too long to be possible, especially as the information gained would probably be of only limited importance in interpreting the trace element analyses.

Trace elements by x-ray fluorescence

The final powders were analysed for trace amounts of lead, zinc, copper, nickel, strontium, rubidium, zirconium, chromium and manganese using a Philips x-ray spectrograph with a universal vacuum attachment (PW 1540) and an electric timer (PW 4062).

Standards

Standards were prepared by the addition method (Ahrens and Taylor, 1961) using pure microcline, biotite and muscovite as the base for three master mixes. A total of 7 different concentrations were used to draw the reference curves. In every case 5,000 ppm of each element were added to the base to make the master mix; portions of each were then diluted with the base to get the desired concentrations, in this way errors in weighing were much reduced.

Contamination

In order to correct for small amounts of contamination from the x-ray anode and tube filament, the intensity of each element line was counted using "spec. pure" SiO_2 and recorded as a fraction of the W Ll line intensity; for each sample the intensity of the W Ll peak was measured and a simple correction for contamination made by the use of this ratio. Only zinc, nickel and copper contamination was detectable and in all cases the amount of contamination was very low and appeared to remain constant with time.

Operating Conditions

The intensity of each peak position was determined in the usual manner by subtraction of the mean background intensity on either side of the peak. The operating conditions were as follows:-

Tube and voltage W target operating at 48Kv and 20MA

Crystal	topaz
Collimator	480 u
Path	vacuum
Counter	scintillation
Fixed time	2 times 90 seconds
Holder	Rotating circular metal with mylar window
Sample state	powder

Element	Zr	Sr	Rb	Pb	Zn	Cu	Ni	W	Mn	Cr
Line analysed	Kal	Kal	Kal	Lal	Kal	Kal	Kal	Ll	Kal	Kal
Low background, 2θ	28.60	36.60	38.80	50.30	63.00	68.60	73.90	76.56	100.30	133.80
Peak position, 2θ	29.85	37.55	39.81	51.28	63.88	69.23	75.39	78.00	101.73	115.35
High background, 2θ	31.12	38.80	40.90	53.30	64.90	70.20	---	---	103.20	116.80

Precision and accuracy

During the course of analysis, 9 replicate determinations were made on both the microcline and the biotite used as the base for the master mix and in each case the samples were remounted in the holder. These determinations were spread over a period of a month and therefore should represent the true variation including any effect due to drift in the x-ray apparatus, changes in packing density after each time the powder is mounted and inaccuracies in reading values from the standard graphs etc.

Table 3 shows the standard and relative deviation of the elements in both feldspar and biotite. Liebhafsky et al (1955) have shown that for x-ray spectrograph data, under ideal operating conditions the standard deviation is equal to the square root of the mean of the total number of counts and therefore as the concentration goes up the standard deviation goes up while the relative deviation goes down. Bearing this in mind, Table 3 shows that, with the possible exception of lead in feldspar the standard deviation is well within usable limits, more especially as in the following sections the data is dealt with in histograms generally having intervals of 20ppm. The detectibility limit is taken, as recommended by Campbell et al. (1959), as a concentration that results in a line intensity equal to 3 times the standard deviation, the detectibility limit for each element being shown in table 4.

Table 5 shows the analysis of 2 standard samples, granite G-1 (recommended values taken from Fleischer and Stevens, 1962) and the M.I.T. biotite (recommended values from U.S. Atomic Energy Commission). With the exception of Pb and Mn the results for G-1 fall within 1 relative deviation (the values for Cu and Ni being so low that comparison is difficult as the relative deviation is very high). The value for Pb is about 50% above the recommended value which compares with similar errors found by M. Kaye using the same apparatus (personal communication) during her work, and in general it is thought that the Pb values, particularly in feldspar could be as much as a factor of two, too high. Table 6 shows five biotites analysed in 3 different ways. The first two analyses are from the Camborne School of Mines, the samples being analysed by A.L. Roberts (personal communication) using a dithizone technique and these same samples analysed again during this study by x-ray fluorescence. The third column in each case is a separate sample, collected by the author from the same quarries and analysed by the same x-ray

Table 3

Standard and Relative Deviation of X-ray Analysis for Nine Replicate Determinations of a Feldspar and Biotite Sample

Feldspar

Element	Mean ($\bar{x}$) (ppm)	Standard Deviation (ppm)	Relative Deviation (%)
Rb	343	± 10.2	3.0
Sr	65	± 4.2	6.4
Pb	55	± 16.1	29.2
Zn	5	± 2.52	51.0
Cu	3	± 2.57	86.0

Biotite

Element	Mean ($\bar{x}$) (ppm)	Standard Deviation (ppm)	Relative Deviation (%)
Rb	848	± 14.7	1.7
Mn	340	± 6.2	1.8
Ni	109	± 4.3	3.9
Zn	52	± 6.9	13.2
Sr	15	± 2.6	17.3
Pb	16	± 4.5	28.1

$$\text{Standard Deviation} = \pm\sqrt{\frac{\Sigma(x - \bar{x})^2}{N - 1}}$$

$$\text{Relative Deviation} = \frac{\text{Std. Deviation}}{\bar{x}} \times 100$$

Table 4

Detectability Limit of Each Element Under the Operating Conditions of this Study

Element	Feldspar (ppm)	Biotite (ppm)	Muscovite (ppm)
Zr	15	5	6
Sr	10	5	5
Rb	10	4	5
Pb	20	3	4
Zn	9	3	3
Cu	13	3	3
Ni	8	3	3
Mn	22	2	2
Cr	14	7	-

Tr = Trace, includes all concentrations between the detectability limit and ½ the detectability limit.

nd = Not detectable, all concentrations below ½ the detectability limit.

- = Not determined.

Table 5

Analysis of 2 Standard Samples, G-1 and M.I.T. Biotite

		Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm
G-1	present study	282	230	83	48	Tr	nd	195	19
	recommended	280 or 250	220	50	40	13	1 or 2	230	22
M.I.T. biotite	present study	8	345						
	recommended	9	447						

Tr = trace

nd = not detectable

Table 6

Comparison Between Dithizone and X-ray Fluorescence Analysis of 2 Samples of Biotite from the same Quarry

Sample and number	Analysed by	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm
C.S.M. 31	dithizone			225	720	15	64	3000
C.S.M. 31	x-ray	nd	1590	nd	370	10	60	2750
P.S. C-28	x-ray	nd	1405	Tr	448	37	46	2700
C.S.M. 32	dithizone			40	920	12	52	3200
C.S.M. 32	x-ray	10	1590	45	340	15	65	2850
P.S. C-25	x-ray	nd	1660	23	438	35	53	3060
C.S.M. 34	dithizone			25	960	16	48	3200
C.S.M. 34	x-ray	Tr	1540	80	395	20	50	2650
P.S. C-24	x-ray	Tr	1525	30	455	37	49	2600
C.S.M. 35	dithizone			25	800	15	56	3200
C.S.M. 35	x-ray	nd	1500	25	385	15	65	2850
P.S. C-50	x-ray	10	1520	40	390	30	70	2900
C.S.M. 36	dithizone			40	840	20	60	3200
C.S.M. 36	x-ray	nd	1360	40	450	15	65	2800
P.S. C-51	x-ray	nd	1360	15	450	15	65	2800

nd = not detected

Tr = trace

C.S.M. = samples collected by Camborne School of Mines and analysed by A.L. Roberts at C.S.M. using the dithizone method and also by the author using x-ray fluorescence.

P.S. = Different samples collected by the author from the same quarries.

fluorescence technique. The figures show firstly, that for the tested elements, with the exception of poor agreement between lead and lack of agreement between zinc analyses that the values obtained by dithizone and x-ray fluorescence compare well, and secondly, that for all tested elements, except for poor correlation in the lead results, the values agree very well between samples taken from the same quarry, indicating that the local variation in the trace element content in this granite is not very important over a short distance. The poor agreement of all lead figures for both x-ray and dithizone reflects its high standard deviation. Although there is close agreement between the two x-ray fluorescence zinc analyses there is a factor of two between the x-ray fluorescence and the dithizone values. There is no easy explanation for this discrepancy but the average zinc values obtained in this work do agree quite well with the average values found by other workers for other granites (see discussion of results), and in the absence of further standard samples these values are taken to be correct within the standard deviations quoted.

Sodium and potassium by flame photometry

Sodium and potassium were determined in all the feldspar samples but because of the number of samples and time required for each determination only a few of the biotite samples were analysed. The method employed was that originally outlined by E.A. Vincent using an Eel flame photometer and is given in appendix 2. Artificial standards as well as Tonalite T-1 (Thomas and Kempe, 1963) and soda feldspar, National Bureau of Standards number 99, (National Bureau of Standards, 1954), were used to calibrate the photometer; the standard curves are shown in diagram 2. The samples were put into solution and stored in polythene bottles to that about 50 samples could be run at one time, a blank was run with each set of samples but was always found to be below the detectability limit. Each solution was burned three times on the photometer, with reference to a standard each time. Distilled water was used to wash out the photometer between each reading.

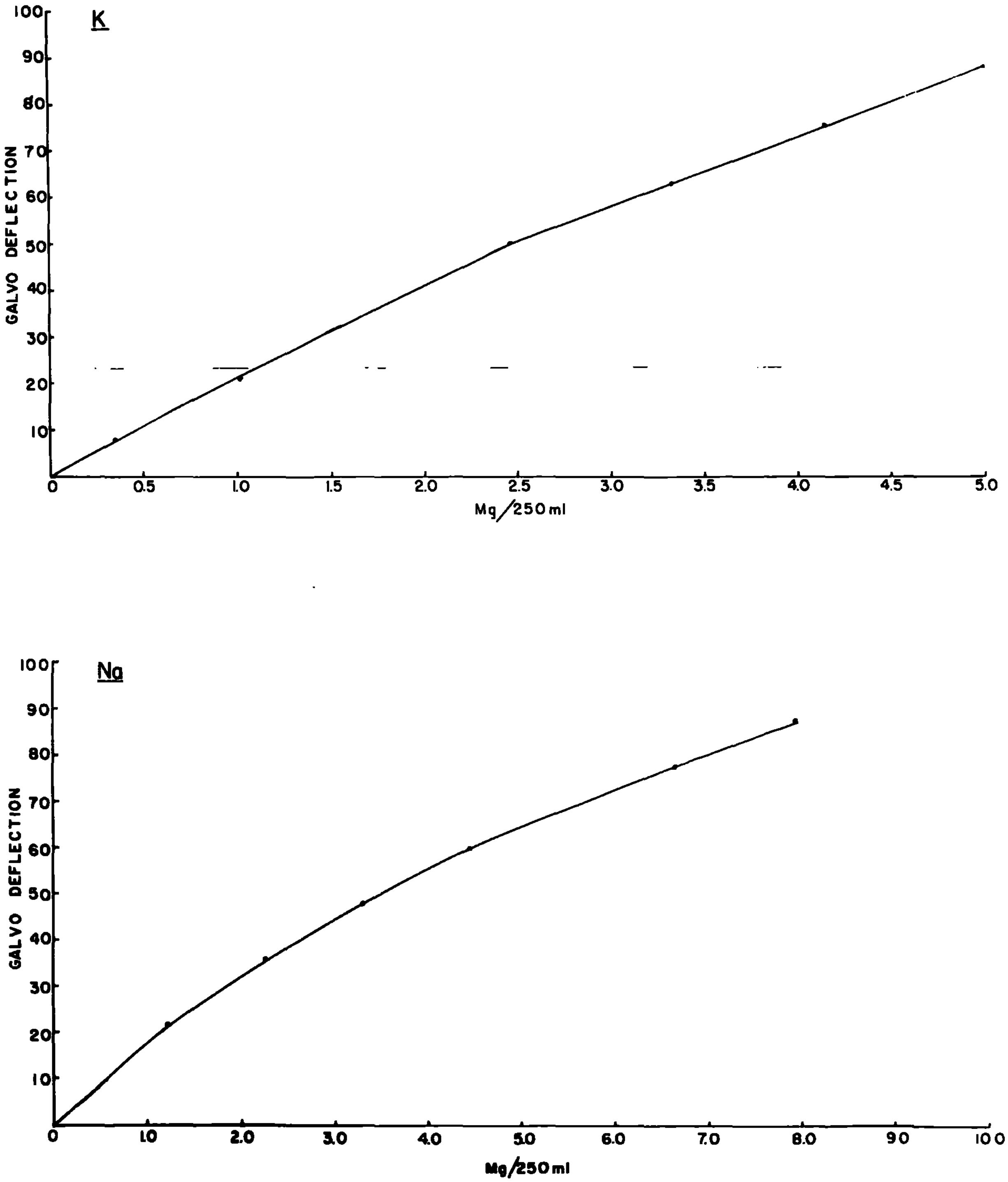

DIAGRAM 2 FLAME PHOTOMETER CALIBRATION FOR Na AND K

Precision and accuracy

Sodium and potassium were determined on several samples which had already been analysed by Pattinson and Stead (11 Queens Terrace, Middlesbrough), R. Lambert, (analyst Durham University Geology Department) and R. Phillips, (Durham University Geology Department). The results are shown in table 7. Four duplicate samples were also analysed and the results are shown in table 8. These two tables show an accuracy of about ± 0.1 to 0.2% and therefore the second decimal place quoted will not normally be significant.

Calcium and Potassium by x-ray fluorescence

Calcium in the feldspar samples and calcium and potassium in the biotites were analysed by x-ray fluorescence. The calcium results appear quite reliable, but the enhancement by calcium of the potassium fluorescent peaks caused errors in the potassium results. However, in knowing the calcium concentration allowances can be made for the amount of enhancement and several checks were made against samples analysed earlier on the flame photometer. While the x-ray fluorescence results for potassium are not as precise as those using the flame photometer, it was felt that the results obtained by this rapid method represent a useful increase in the amount of information available. A set of standard curves was established as shown in diagram 3 by using a set of artificial mixes with known amounts of calcium and potassium. Knowing the calcium concentration, the potassium concentration is read off the appropriate line.

Operating conditions

In all cases, for both potassium and calcium a standard was kept permanently in a holder and counted after each sample, the ratio of sample counts to standard counts was then used. In this way drifts in the flow counter etc. were corrected for. No fluctuations of more than 1% occurred over a 12 hour working period, and generally fluctuations of 0.1% or less could be expected. Background values were obtained in all cases but seldom came to more than 1% of the peak intensity.

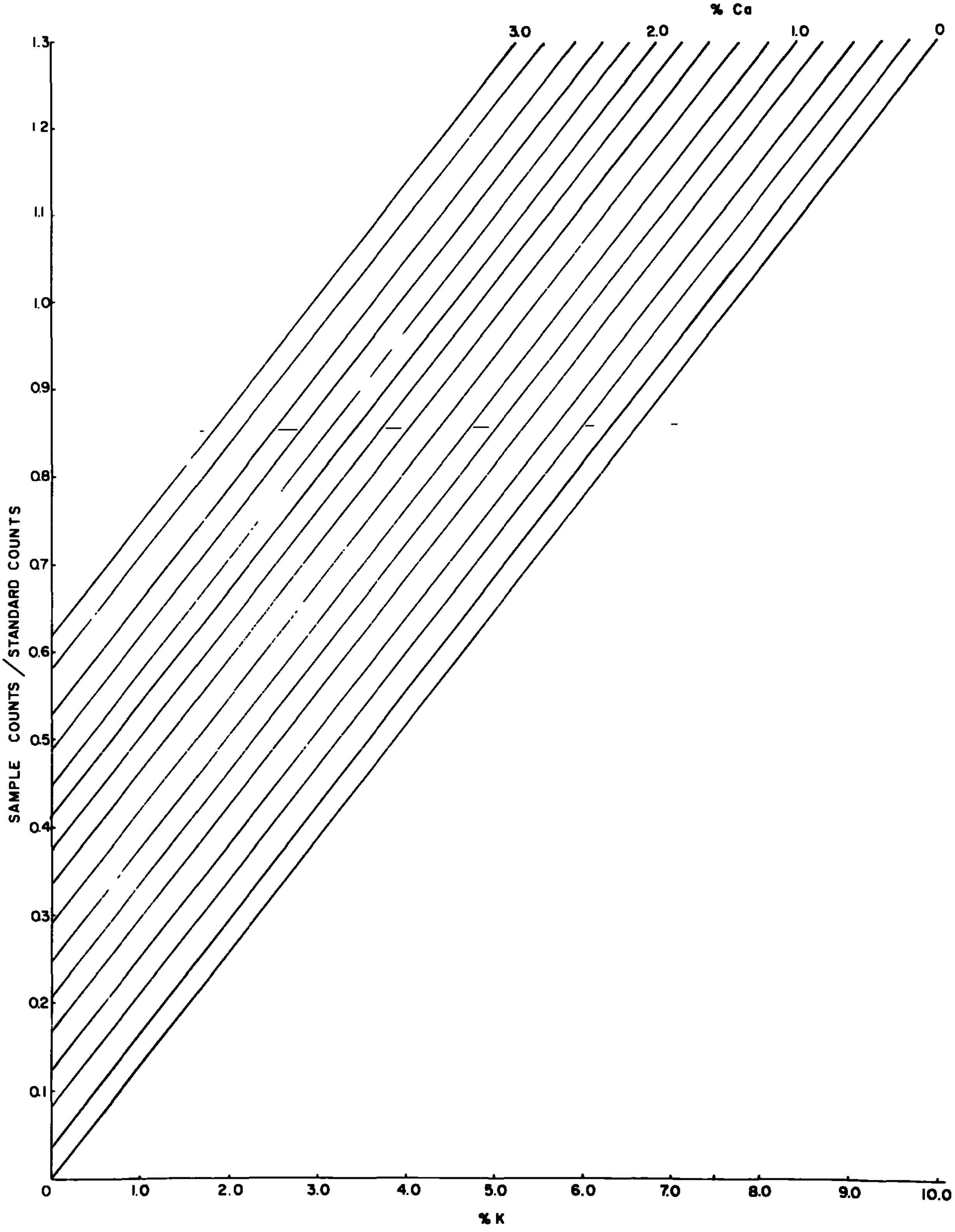

DIAGRAM 3 STANDARD CURVES FOR K IN BIOTITE BY X-RAY FLUORESCENCE

Table 7

Sodium and Potassium Results for Previously Analysed Samples

		P. & S.	R.L.	R.P.	Present study
Rookhope borehole 1281'6" (granite)	Na(%)	0.21	0.15	-	0.18
	K(%)	5.96	6.55	-	6.22
Rookhope borehole 1358' (granite)	Na(%)	1.63	2.00 & 2.10	-	2.05
	K(%)	6.10	6.29 & 6.55	-	6.20
R-80 Sample from Cleveland dyke collected by R. Phillips	Na(%)	-		2.57	2.69
	K(%)	-		2.16	2.35

P. & S. = Analyses by Pattinson and Stead

R.L. = Analyses by R. Lambert (Durham University Geology Dept.)

R.P. = Analyses by R. Phillips (Durham University Geology Dept.)

\- = Not determined

Table 8

Duplicate Determinations of Sodium and Potassium

Sample No.	Na(%)	K(%)
E-1	4.38	1.69
	4.45	1.75
E-8	3.59	2.14
	3.79	2.32
E-9	3.89	2.78
	3.92	2.94
C-23	2.58	4.07
	1.87	4.18

Tube and voltage	Cr target operating at 40 Kv and 20 MA
Crystal	E.D.D.T.
Collimator	480 u
Path	vacuum
Counter	flow using a gas of composition 90% Argon, 10% Methane
Fixed time	2 times 60 seconds
Holder	Rotating circular metal with mylar window
Sample state	powder

Element	Ca	K
Line analysed	$K\alpha_1$	$K\alpha_1$
background 2θ	12.80	12.80
Peak position, 2θ	14.80	20.28

Precision and accuracy

Unfortunately there were no available samples of feldspar for which calcium and potassium had already been determined, and because of the matrix effect while analysing for such light elements the comparison with a granite would have little meaning. However, potassium had been determined in several biotites and the comparison between the two methods is shown in table 9. With the exception of 2 results (D-9 and M.I.T. biotite) they are in very close agreement.

Modal analysis

To aid a more detailed interpretation of the trace element concentrations in the composite rock powder, an estimate of the concentrations of the mineral percentages (microcline, orthoclase, plagioclase and quartz) in the analysed powder was required. A method for determining the concentrations of the minerals directly (i.e. the mode) was considered superior to the recalculation from a chemical analysis (i.e. the norm.). Point-counting, infra-red spectroscopy and x-ray diffraction were all used quantitatively. The latter proved to be the most useful.

Point-counting

Table 9

Comparison between X-ray Fluorescence and Flame Photometer Determinations of Potassium in Biotite

Sample No.	X-ray (%)	Flame photometry (%)
C-49F	6.3	6.41
C-49E	7.3	7.17
C-49D	4.2	4.00
C-49C	6.7	6.88
C-49B	5.3	5.10
A-4	6.3	6.44
A-24	5.8	5.81
S-11	4.7	5.01
S-16	4.7	4.70
D-9	5.4	6.36
D-4	5.8	5.89
M.I.T biotite	9.8	7.50 (recommended)

To alleviate the problem of counting a coarse grained porphyritic rock, and to allow for the preferential concentration of one mineral in the analysed powder due to differential grinding and/or separation, a point count of the powder to be analysed was considered superior to a point count of a rock slice or a thin section. To allow the identification of the two feldspars in the powder the feldspars were first stained.

Staining procedure

Both the K-feldspar and the plagioclase were stained following the process outlined by Bailey and Stevens (1960), but, the process had to be altered slightly in order to stain mineral grains rather than rocks or thin sections.

About 0.5 grammes of the sieved homogeneous powder (between 58 and 155 mesh) were selected and placed in the bottom of a tall, 200 c.c. teflon beaker, and completely covered with concentrated hydrofluoric acid for 2 minutes. After 2 minutes a gentle stream of cold water was directed into the beaker and allowed to run for 4 to 5 minutes, the excess water spilling over the edge. Care was taken to ensure that the water pressure was not strong enough to wash any of the grains out of the beaker. After the grains had been washed completely free of hydrofluoric acid they were caught in a 200 mesh nylon sieve, and holding them in this sieve they were then treated as outlined in Bailey and Stevens (1960).

After a little practice it was found unnecessary to stain the plagioclase as its opaque appearance made it easily distinguishable from the clear quartz and yellow K-feldspar.

Counting

The stained mineral grains were spread, one layer thick over a glass slide and put under a petrographic microscope fitted with a point-counter. At least 1000 points were counted for each powder.

Results

Although the method appears reasonably accurate, it is very time consuming, destroys the sample for further chemical analysis, samples only a very small proportion of the total rock powder and does not distinguish between microcline and orthoclase. A more rapid method was sought which did not include these disadvantages.

Infra-red Spectroscopy

The qualitative and quantitative application of infra-red spectroscopy to organic and other non-silicate substances has been in common use for some time. It is only more recently that this technique has been applied as a qualitative method (Launer, 1952; Laves and Hafner, 1956 and 1963; and Hafner and Laves, 1957), and a quantitative method (Hunt and Turner, 1953; and Lyon et al., 1959) to naturally occurring silicates. A total of 51 infra-red curves of "standard samples" were run in order to establish the accuracy of the quantitative method.

Theory

The atoms of a solid are constantly vibrating around the equilibrium position at frequencies between 10^{12} and 10^{14} cycles/second. Because infra-red rays also have frequencies in this range it is possible to determine some of the vibration frequencies of the solid. When infra-red light is passed through a substance, if its wavelength coincides exactly with the vibration frequency of any 2 atoms or molecules in the structure, absorption will take place. This absorption always occurs at the same characteristic frequency, and the concentration which is directly proportional to the optical density (O.D) is expressed by the equation:-

$$O.D = \log_{10} {}^{Io}/_{I}$$

Io = incident light intensity

I = transmitted light intensity

Each compound will have its own characteristic absorption pattern, depending on the elements present, and their type of bonding. Launer (1952) gives the position of the absorption bands for 18 silicates, and shows a regular variation with the different O - Si groupings.

It has also been shown that a shift of a characteristic peak may occur with composition changes in an isomorphous series. For example, Thompson and Wadsworth (1957) found that one absorption band shifted regularly with changing anorthite composition of plagioclase. This method has the added advantage of being apparently independent of high or low temperature forms.

Hunt and Turner (1953) applied infra-red spectroscopy to the quantitative determination of quartz, orthoclase and dolomite, while Lyon et al. (1959) did a quantitative analysis of microcline, quartz, and plagioclase in the same rock powder.

Technique

The standard procedure for making potassium bromide discs was employed. The original powder was ground in a tungsten-carbide vial, sieved to below 150 mesh and about 5 grammes ground again for a further 30 minutes. One quarter of a milligramme of crushed sample was weighed out using a White Electrical Instruments Incorporated torsion balance, and mixed thoroughly with 1 gramme of potassium bromide in an agate mortar. Launer (1952) emphasized the fact that if the grain size was greater than 5 microns refraction around the grains will occur, causing poor peak resolution and a high background. The grinding method employed was found to be satisfactory but not ideal. The potassium bromide and sample mixture was put in a stainless steel vacuum die (15 millimetres in diameter), giving a sample concentration of 0.82 milligrammes per square centimetre. The die was evacuated for 3 minutes and then a pressure of 12 tons per square inch applied for 10 minutes. The infra-red curve of the resulting pellet was obtained on a Grubb-Parsons "Spectromaster" infra-red spectrophotometer. The samples were scanned from 12 to 25 microns at 2 minutes per micron using slit programme number 10 at normal gain. The chart speed was 2 inches per micron.

A series of artificial mixes, using only 2 of the 4 end members at any one time, were made. After mixing a total of about 4 grammes of the pure end members together to get the desired proportions, 0.25 milligrammes were weighed out and analysed. Several mixes consisting of 3 end members (K-feldspar, quartz and plagioclase) were made to give further control.

Results

Diagram 4 shows the traces of the end members, microcline, orthoclase, plagioclase and quartz. Initially the results were determined using the same method and peaks as Lyon et al. (1959), i.e. the percent transmission of the 12.45u and 14.41u peaks for quartz, 13.48u for oligoclase and 13.76u for microcline and orthoclase. These peaks however, were found to be unsatisfactory and gave poor results. The quartz peak at 12.45u disappears if quartz falls below 50% of the total, and the plot of percent transmission of the 14.41u peak vs percent quartz gave erratic results and errors of 10% are common. The height of the oligoclase peak (13.48u), and therefore the optical density was found to vary with the high and low temperature forms as shown by the heating experiments of Laves and Hafner (1956). This applies to all oligoclase peaks. It was found also that the optical density of all the K-feldspar peaks increases with triclinicity independent of the K-feldspar concentration. This observation is also reported by Liese (1964) and Hafner and Laves (1957) and can be seen by coparing the traces for microcline and orthoclase (diagram 4). It appears, therefore, that unless all the K-feldspar is known to be either microcline or orthoclase, and all the plagioclase is known to be either high or low form, a precise quantitative determination of K-feldspar and plagioclase concentrations based on optical density is impossible. Even if these factors are known, the peaks are all relatively small and therefore even under ideal conditions the precision will be low. As most of the rocks examined were known to have a mixture of orthoclase and microcline the application of this technique for quantitative determinations of K-feldspar and oligoclase was not feasible.

From diagram 5 it can be seen that there is a regular shift of two characteristic peaks with changing composition, i.e. the split of the 13.0u and 13.75u K-feldspar peaks to the 12.7u,13.2u, 13.5u and 13.8u peaks of plagioclase with increasing concentrations of plagioclase. While Hafner and Laves (1957), show a slightly greater and more regular variation of peak position with changing K-feldspar and plagioclase composition, their observations could not be reproduced exactly here.

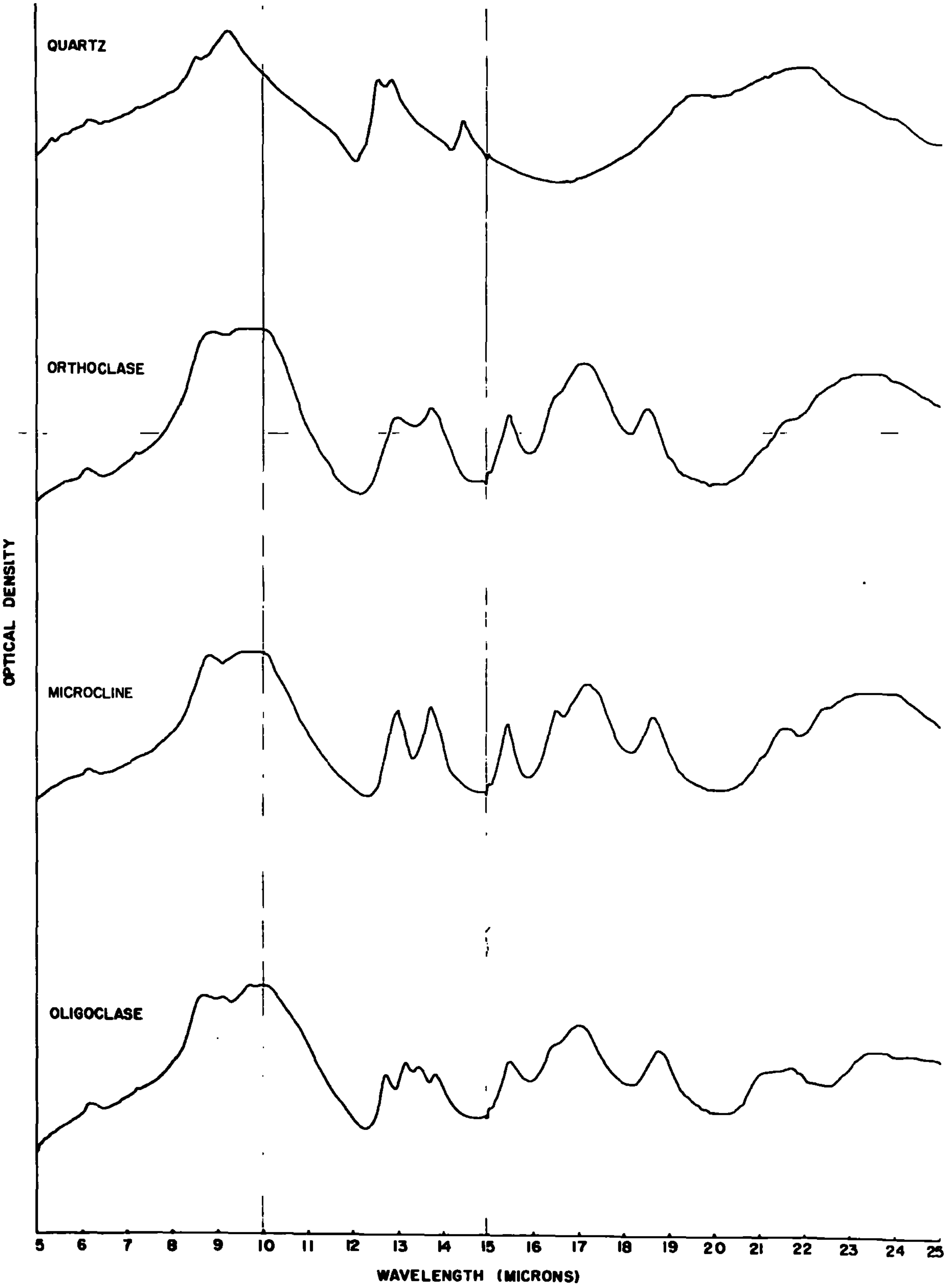

DIAGRAM 4 INFRA-RED CURVES FOR PURE MINERALS

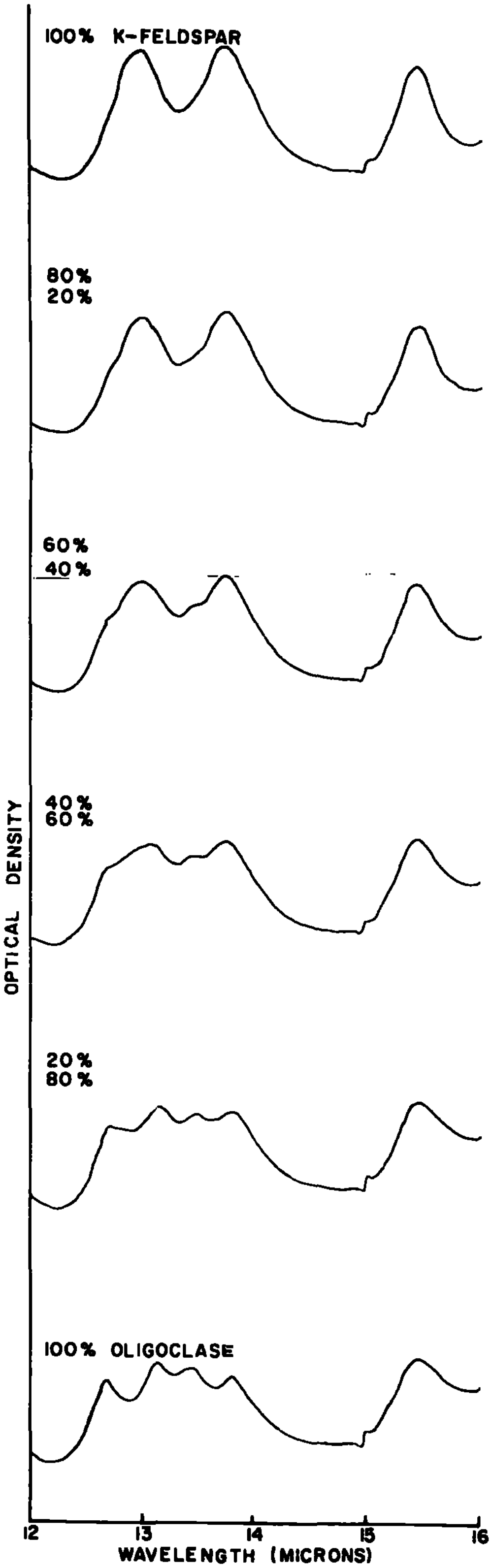

DIAGRAM 5 INFRA-RED CURVES FOR CHANGES IN K-FELDSPAR – OLIGOCLASE CONCENTRATION

It was originally hoped to use such peak shifts as a quantitative measure, but taking into account in particular shifts in peak position shown by Thompson and Wadsworth (1957), for changes in An composition, and also the reproducibility of the peak positions for the same mixes run several times, it was found that this method was unreliable.

Especially after considering the error shown by Lyon et al. (1959) in their analysis of G-1 (table 10) it was decided to develop the diffraction technique in preference to the infra-red as an analytical tool.

X-ray Diffraction

The use of the intensity x-ray diffraction lines as a quantitative measure of the minerals present in a powder was suggested as long ago as 1919 by Hull. However, it was not until the more complete work of Clark and Reynolds (1936) that this idea was used extensively. The early workers relied on the microphotometric calculations of line intensities on film, and it was not until the advent of the geiger counter in 1945 that the present, reasonably precise method developed. Klug and Alexander (1954) gave a review of this method, and showed that an accuracy of ± 5% of the amount of the mineral present is quite possible. More recently Tennant and Berger (1957), Diebold et al. (1963), and Otalora (1963, personal communication) have used this technique, and all report an accuracy of about ± 5%. However, all the workers seem to have applied this method to carbonate rich rocks only. No recorded instances of determining quartz and feldspar concentrations were found.

Technique

Standard curves were constructed using the same "standard mixes" as employed during the infra-red investigation, i.e. mixing the pure end members two at a time, to get the desired ratios. Sufficient of each mix (about 4 grammes), was used to fill three cavity mounts. These were scanned in turn on a Philips PW 1010 diffractometer using generator PW 1010/25 and Goniometer PW 1030/30, over the desired angles, the pulses being recorded by an automatic chart recorder. The heights of the analysed peaks were measured and the average of all three readings taken. The results were

Table 10

Infra-red determination of the mineralogical composition of G-1 by Lyon et al. (1959).

Mineral	G-1 recommended	Infra-red (3 separate runs)		
Quartz (%)	27.7	37	36	35
K-feldspar(%) (microcline)	34.1	30	28	28
Plagioclase(%) (An_{26})	31.3	22	22	25
Biotite(%)	3.5	nd	nd	nd

nd = not detected

plotted as shown in diagrams 6 and 7.

Operating conditions

Tube and voltage	Cu target operated at 40Kv and 20 MA
Filter	nickel
Slits	Divergence 1°, receiving 0.1°, scatter 1°
Scan speed	½° (2θ) per minute
Chart speed	times 20 or 800 millimetres per hour giving 10 chart divisions for 1°(2θ)
Rate meter	4
Time constant	8
Multiplier	1
Counter	proportional counter at 1730 volts
Discriminator	amplitude 23.2 volts channel width 8 volts attenuation 4 volts

These operating conditions were found to give a background of about 5 chart divisions while the most intense peak did not generally exceed the limits of the chart. For peaks greater than 100 chart divisions under these conditions the rate meter was changed to 8 and then the peak height bled? measured and the value halved for comparison with those peaks measured at rate meter 4.

Peak Positions

It was found most convenient to measure the K-feldspar, plagioclase, quartz ratio first, and then measure the microcline, orthoclase ratio afterwards. The height of the plagioclase $\bar{2}01$, quartz 100, and orthoclase $20\bar{2}$ plus microcline 111 gave the plagioclase : quartz : K-feldspar ratio, while the height of the orthoclase 111 and microcline 111 gave the orthoclase : microcline ratio. It was also possible to measure at the same time the obliquity of the K-feldspar by the separation of orthoclase 111 and microcline $1\bar{1}1$ peaks (MacKenzie, 1954), and the albite composition of the plagioclase by the separation of the $1\bar{3}1$ and 131 peaks, (Smith and Yoder, 1956).

Results

From diagrams 6 and 7 the K-feldspar/oligoclase, oligoclase/quartz and quartz/K-feldspar ratios are determined, giving 3 equations in 3 unknowns from which the percent of K-feldspar, oligoclase and quartz can be determined. Using diagrams 7 the microcline/orthoclase ratio can also be calculated. Table 11 gives the determined values of several artifical mixes whose known weight percents are shown in the right hand column.

Precision

It can be seen from table 11 that all the results fall to within ± 6% of the amount present, and that the majority fall within ± 4%. While a higher precision can be obtained by rotating the samples during measurement and by taking the average of 10 rather than only 3 determinations of each peak, the results were considered suitably accurate for the present purpose. It will be noted that the K-feldspar-quartz graph is a curve, indicating that quartz is absorbed by K-feldspar. It is possible by the use of an internal standard (see Klug and Alexander, 1954) to get straight line graphs in these cases. However, because the precision was within acceptable limits this precaution was unnecessary.

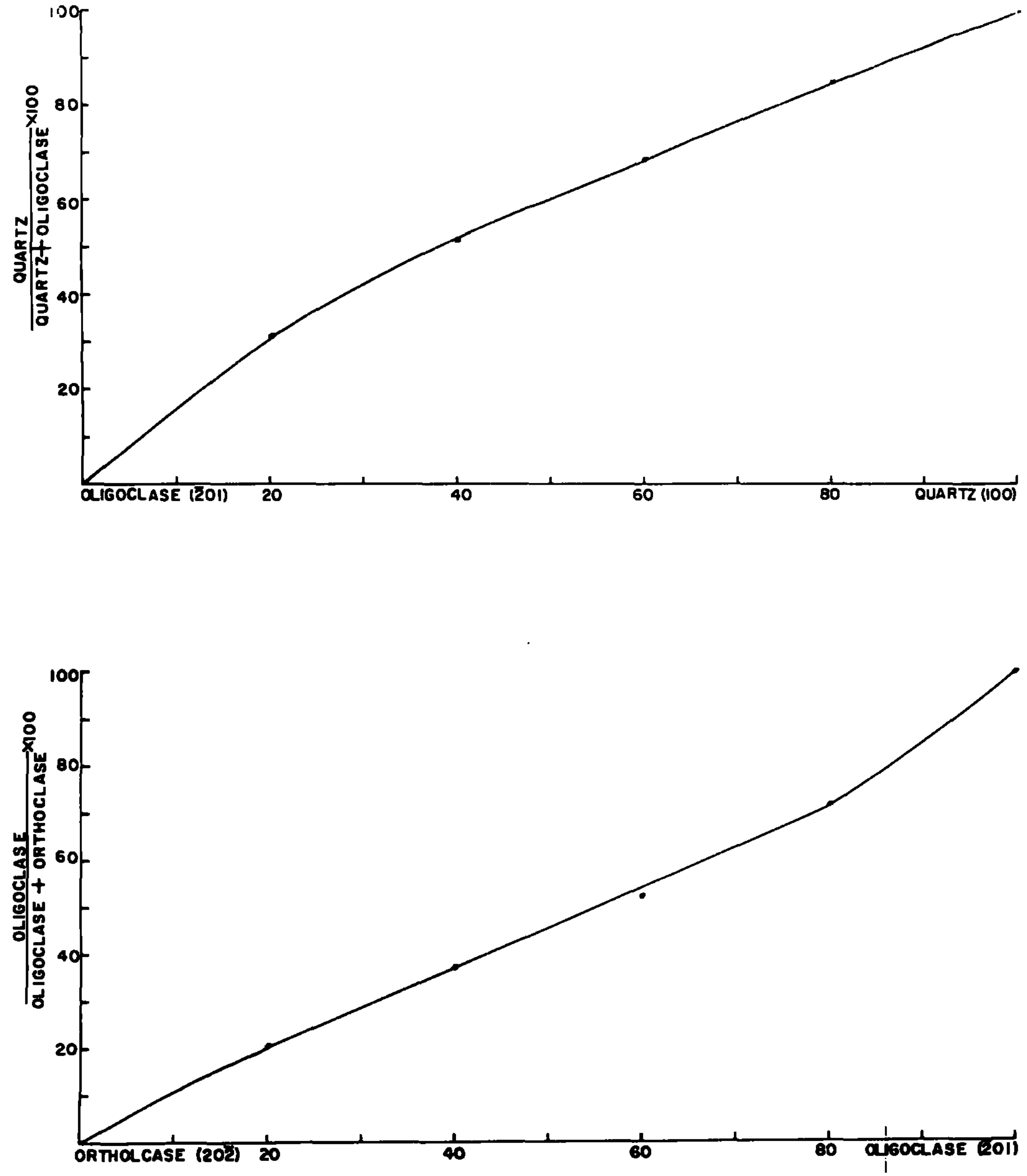

DIAGRAM 6 RELATIVE INTENSITY OF X-RAY DIFFRACTION PEAKS

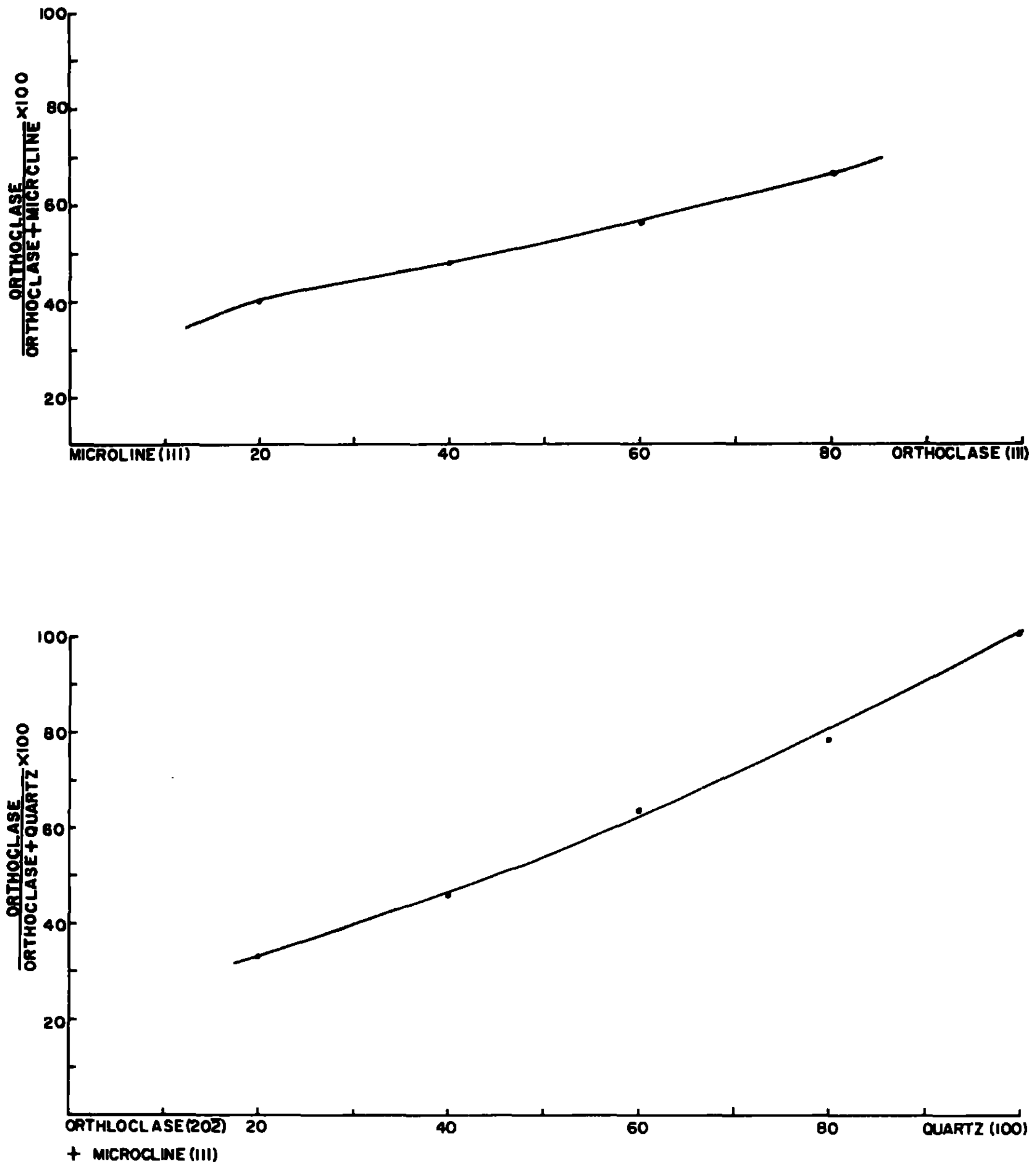

DIAGRAM 7 RELATIVE INTENSITY OF X-RAYDIFFRACTION PEAKS

Table 11

Mineral Percentages Determined in several Standard Samples by X-ray Diffraction

Mineral	Artificial Mix (%)	X-ray diffraction(%) 2 determinations		Difference of Average (absolute %)
Quartz	20	23	25	4
Orthoclase	50	50	47	1
Oligoclase	30	26	28	3
Quartz	10	15	17	6
Orthoclase	40	34	38	4
Oligoclase	50	50	47	1
Quartz	33	39	38	6
Orthoclase	33	33	33	0
Oligoclase	33	27	28	5

Chapter 3

Results and Discussion of Results

During the present study 164 samples were analysed and of these 27 had sufficient concentrations of muscovite, 117 sufficient biotite, and all sufficient feldspar plus quartz for analysis. A total of 3,026 analyses are recorded. An additional 656 estimates of mineral concentrations were made by x-ray diffraction on the 164 feldspar plus quartz fractions. The sample locations and results of the analyses are given in appendix 1, while a compilation of the results is given as histograms in diagrams 8 to 22, where in each case the arithmetic mean is indicated by an arrow.

All values for the feldspar plus quartz fraction were corrected, assuming that the quartz was free from all elements analysed for in this study. In this manner comparison between two samples with very different quartz contents could be made. All values shown in the histograms and quoted in appendix 1 have been corrected. The validity for making this assumption was tested by hand picking sufficient quartz for analysis from two different samples and in each case all elements were found to be below the limit of detectability.

The results are discussed under three different headings, the first of which concerns each element in turn and its variation with respect to all granites studied, the second a short description of each region and any major or trace element variations which apply only to that region, and the third, the change in trace element concentration away from mineral veins with reference to samples analysed from Geevor Mine, Cornwall.

Element distribution

For a proper understanding of the regional studies the element variation with respect to all granites examined is a great help, this aspect being dealt with first. In this section constant reference is made to the arithmetic mean or averages of a trace element population in a granite stock, but it must be emphasized this is only a convenient method to give a quick indication of the trace element population and for a more accurate and detailed picture, particularly to see the spread of results, the reader should refer to the histograms.

The term granite is used for plutonic rocks ranging in composition from tonalite to granodiorite to granite i.e. the normal calc-alkali range.

Calcium

From diagram 8 which includes a histogram of the calcium analyses in feldspar, it can be seen that the arithmetic mean of all the Cornwall samples is 1.09%, while the means for the different stocks of this area vary between 0.68 and 1.33%. In comparison the feldspars from all the other granites (with the exception of the Weardale granite which averages 1.06% calcium) are at least a factor of two richer in calcium, a difference which is clearly significant.

Although the biotite analyses are by no means complete, those results listed in appendix 1 show an arithmetic mean of 0.38% and 0.39% for the Cornwall and Weardale samples respectively, while the other granites range between 1.06% and 1.66%. This again shows a clearly significant difference of at least a factor of two.

Sodium

The sodium results for the feldspars (diagram 8) show a greater uniformity than do the calcium results, but a division between the Cornwall and Weardale samples on one hand and the rest of the granites on the other, is still evident. The difference of 50% between the average for Devon and Cornwall and the highest Caledonian granite (Shap) may be significant, but the other differences are almost certainly not.

In-sufficient sodium analyses were made on the biotite samples to allow comment.

Na/Ca ratio in feldspars

The sodium and calcium concentrations are given in diagram 8 while the arithmetic mean of the Na/Ca ratios are given in table 12. These

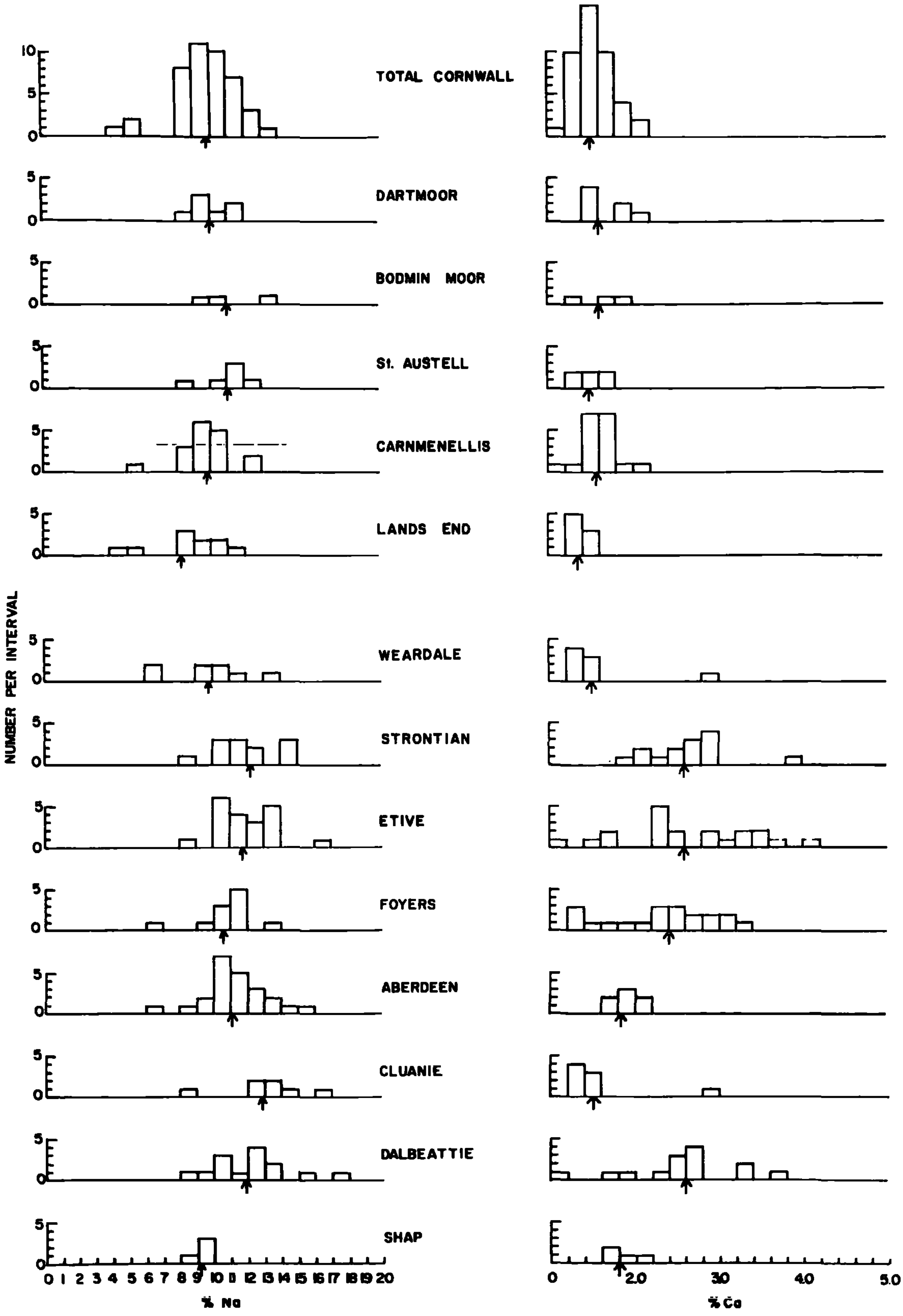

DIAGRAM 8 Na AND Ca ANALYSES IN FELDSPAR

Table 12

The mean Na/Ca ratio in Feldspars from Different Granites

Granite Stock	Na/Ca ratio
Dartmoor	3.74
Bodmin Moor	4.29
St. Austell	5.34
Carnmenellis	4.18
Lands End	5.96
Average for all Cornwall	4.52
Weardale	4.59
Aberdeen	2.11
Etive	1.82
Dalbeattie	1.78
Cluanie	3.51
Strontian	1.89
Foyers	1.51
Shap	2.26

figures show a clear division between the Cornwall and Weardale granites (4.52 and 4.59 respectively) and the remainder of the granites analysed (ranging between 1.51 and 3.51).

Potassium

As shown by the histograms in diagram 9, quite a clear division appears again between the Cornwall and Weardale samples, and the others. A significant difference of 100% exists between most of the stocks in these two areas except the Shap analyses which fall fairly close to those of Cornwall. The biotite analyses demonstrate the same division with a clear 60% (or 96% probability) difference in all cases except Shap.

The major element analyses reflect differences in the composition of the rocks which is evident from their modal composition and the classification names given to them. A finer division than the two groups already mentioned appears possible although the division is not in every case statistically significant. The trend however, as demonstrated by all three major element concentrations and the Na/Ca ratio does follow the rock type; i.e. the Weardale and Cornwall granites fall into one group, the Scottish granodiorites (with minor tonalite) into a second group, and the Shap adamellite intermediate between these two.

The classical theories of igneous rock genesis generally regard increases in the sodium and potassium concentrations and reduction of the calcium as a function of fractionation of a magma. While fractionation does undoubtedly occur whether or not it was operative during the formation of the granites under investigation remains to be proved. It is possible that differences in the element composition are partly or wholly a function of differences in the original composition of the "parent rock". It is from the associated trace elements that further information can be derived; if the present major element composition is due to original differences in the parent rock the trace elements would be expected to show more or less random concentrations. Alternatively, if fractionation has taken place the trace elements would be expected to fall on the smooth "liquid line of descent" already established from other areas where

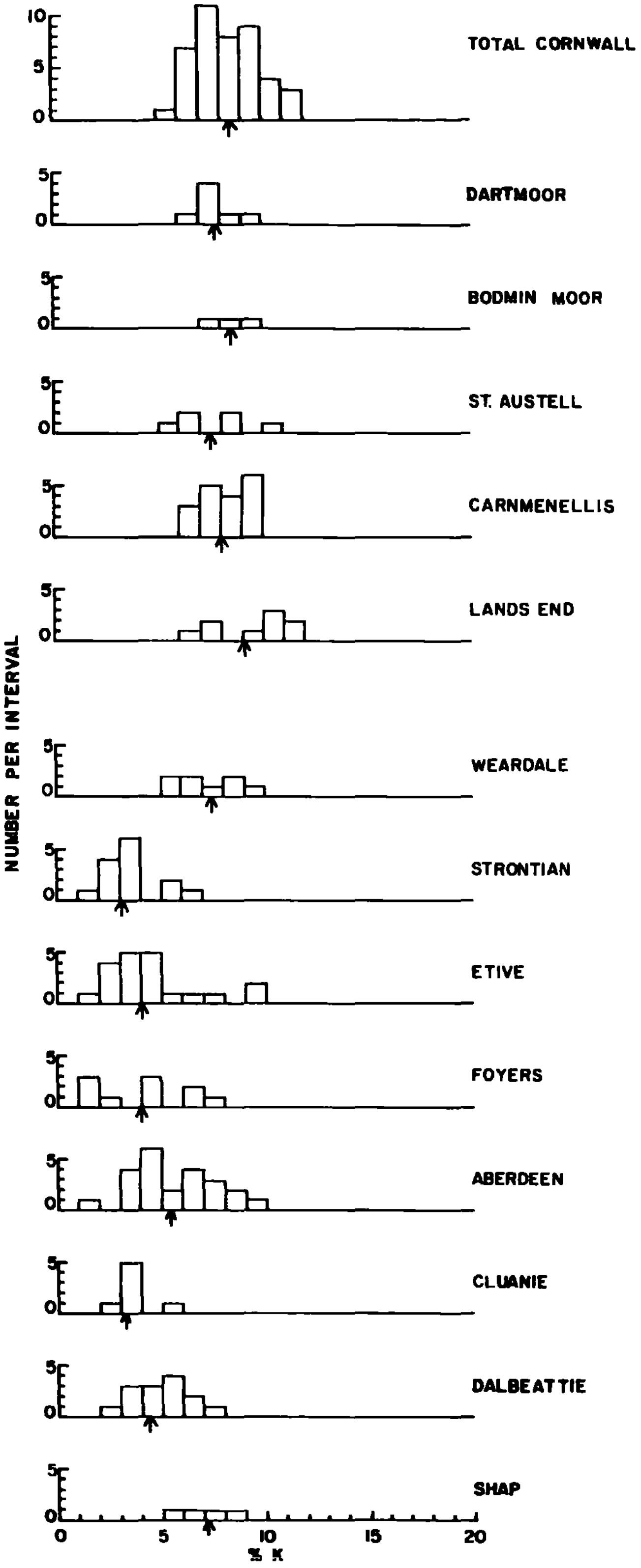

DIAGRAM 9 K ANALYSES IN FELDSPAR

the observed development of successively fractionated rocks can be studied quite closely. In order to see if these patterns are repeated here the non-heavy metal trace elements are discussed next.

Rubidium

Diagram 10 is a histogram of the rubidium analyses for feldspar and biotite, and diagram 22 the analyses for muscovite. From these diagrams it can be seen that the rubidium concentration in the feldspars from Cornwall and Weardale averages about 900ppm this being a factor of $2\frac{1}{2}$ higher than the next highest rubidium concentration, (which is found in the Shap granite), and therefore represents a significant difference. For biotite the picture is much the same, but only the Cornwall samples are relatively enriched in rubidium (three times higher than the next highest, Shap), and the Weardale samples are lower and generally about the same as the remainder of the granites. The muscovite analyses show the Cornwall samples to be twice as rich in rubidium as those from Weardale.

Although the information for the Weardale granite is conflicting, the Cornwall analyses show a definite increase in rubidium over all other areas which would indicate that the Cornwall granites have undergone greater fractionation than the other granites. This observation is based on the works of other authors such as Sen et al. (1959) and Wager and Mitchell (1951) etc., who report an increase in rubidium as fractionation proceeds.

K/Rb ratio in feldspars

In 1952 Ahrens et al. showed from a consideration of about 100 determinations in several different rock types, including granite, that all the K/Rb ratios fell within quite narrow limits. Since then more than 1000 analyses from all rock types have been made and found to lie within the same limits (Taylor and Ahrens, 1959). Taylor and Heier, (1958), found a similar close relationship in the K/Rb ratio of both potassium and alkali feldspars from Pre-Cambrian rocks of Norway with the exception of those samples from pegmatites where the K/Rb ratio was

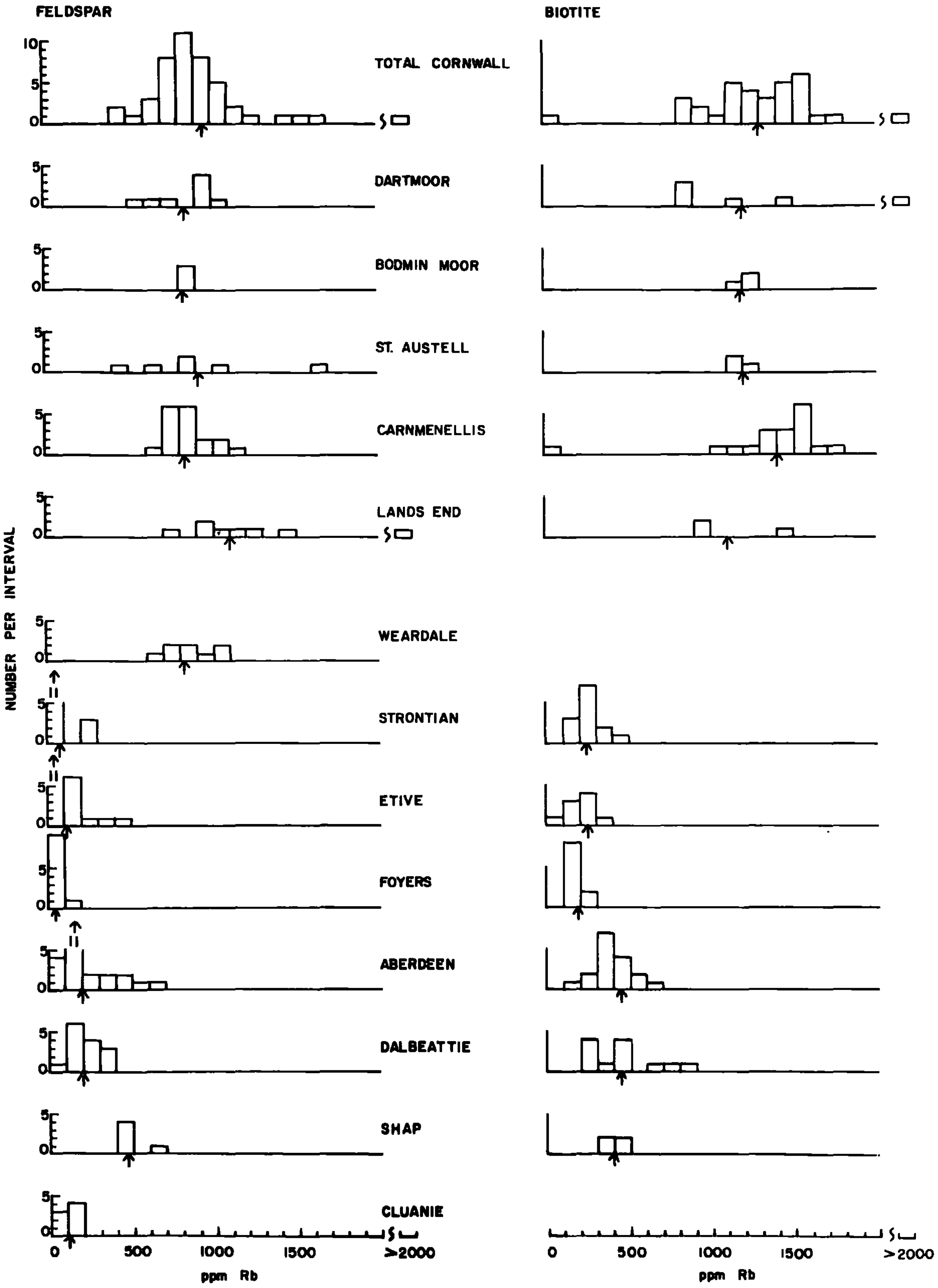

DIAGRAM 10 Rb ANALYSES

considerably lower than the average established by Ahrens (i.e. Rb rich) and fell outside the limits of scatter established by him. Bearing in mind Goldschmidt's two rules (Goldschmidt, 1954), this is exactly the effect which would be expected in highly fractionated rocks. Taylor and Heier also found a small group of samples which fell in the rubidium poor part of the field, again outside the normal limits of scatter. There appear to be two possible reasons for this:- 1. that the number of co-ordination sites for potassium was limited and that the 11% difference in size became critical; (Taylor and Heier, in their study, found the rubidium poor samples to be in fact slightly higher in plagioclase than the others). 2. A purely structural explanation is not sufficient and an additional factor seems to be the concentration of potassium in the system from which the feldspars are crystallising; this natural excess may become effective in allowing the potassium to obtain more of the crystal lattice sites. Heier and Taylor in a later paper (1959a), reconfirmed their earlier observations with more analyses.

Diagram 11 shows a plot of the log ppm rubidium versus log percent potassium for feldspar samples analysed during the present study and the limits of scatter (solid lines) found by Ahrens et al. (op.cit). From this diagram it can be seen that there are three main areas:- 1. the Cornwall and Weardale samples fall in the rubidium rich area just outside Ahrens limits of scatter (similar in position to the pegmatites analysed by Taylor and Heier (op.cit)). This agrees with analyses carried out by Taylor et al., (1956), on samples from several granite bodies including unaltered granite from St. Austell. The results for St. Austell determined in the present work coincide with those Taylor et al. obtained. 2. includes the bulk of granites analysed and falls within Ahrens' limits of scatter. 3. includes most of the Strontian, Foyers and Etive samples showing considerable scatter in the rubidium poor area.

Diagram 11 shows that far from fitting Ahrens' limits of scatter around a constant K/Rb ratio the present results indicate a continually changing K/Rb ratio in a line diagonally across Ahrens' limits. A compilation of all the available K/Rb analyses given by Heier and Adams (1964, diagram 12) shows a very similar trend, particularly when both

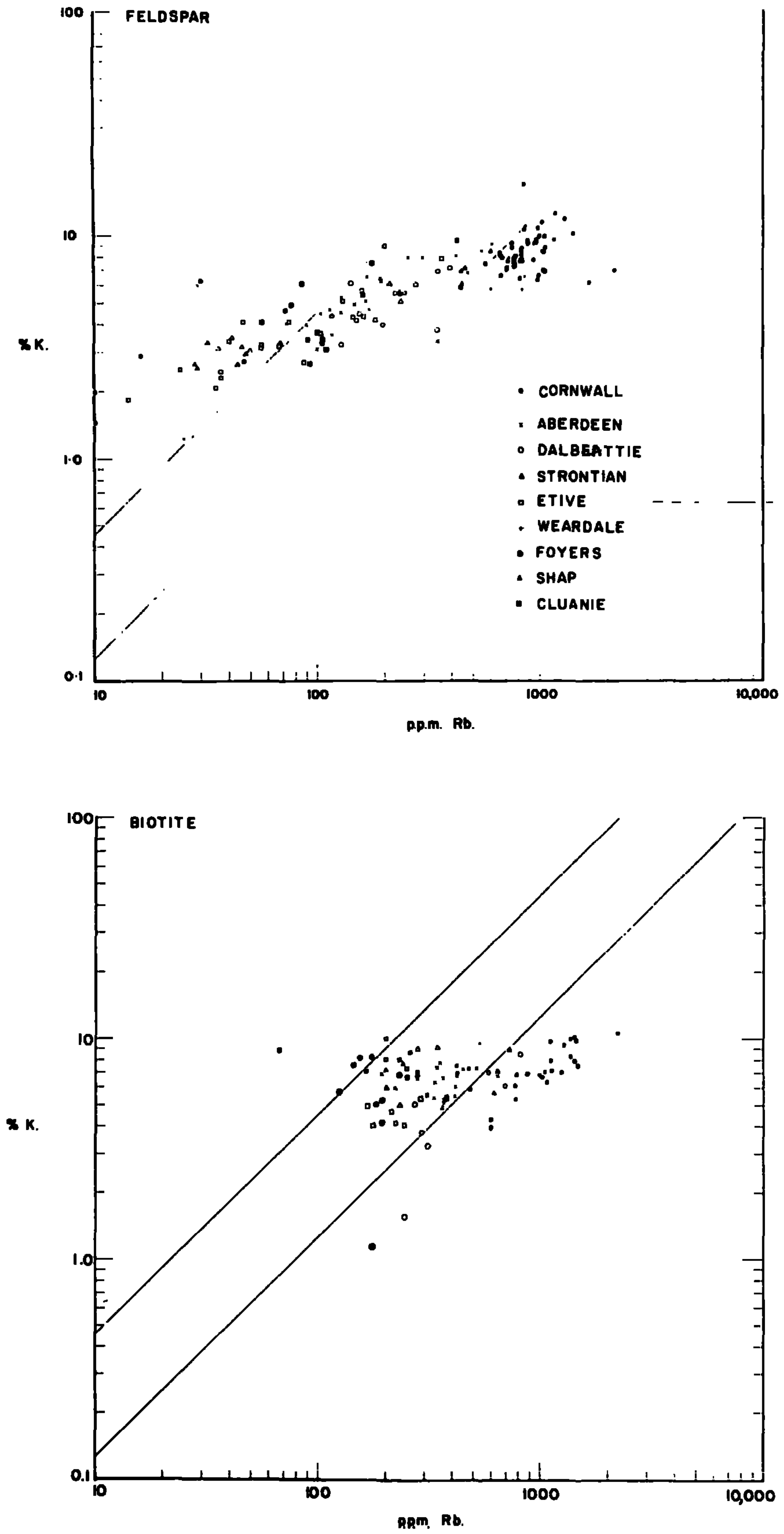

DIAGRAM 11 PLOTS OF K vs Rb IN FELDSPAR AND BIOTITE

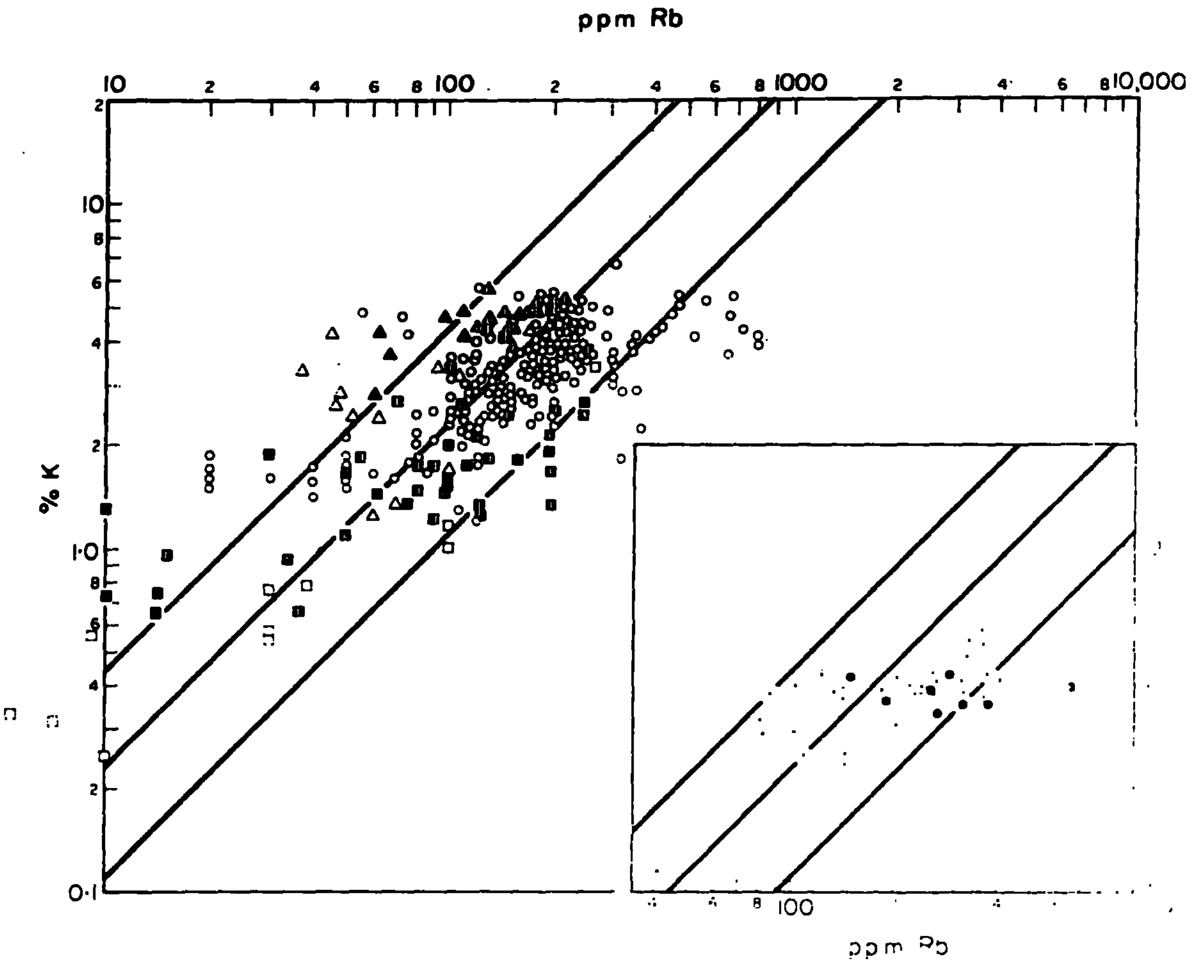

DIAGRAM. 12: Plots of Rb vs. K in plutonic rocks. (AFTER HEIER AND ADAMS)

· gabbroic rocks (8, 11, 12, 17)
■ diorite and qtz. diorite (7, 11, 12, 13, 17, 22)
△ Monzonite (11, 12)
▲ syenites (12, 22)
"granitic" rocks (2, 5, 6, 7, 9, 11, 12, 13, 17, 19, 21)
● riebeckite soda granite (12, 22)
·· nepheline syenite (10, 23)

the granite and granodiorite analyses are considered, as in the present study. In their diagram Heier and Adams show 22% of the analyses falling outside Ahrens' limits of scatter. Further plots of acid rock analyses in the same paper show a similar cross-cutting trend very clearly. While the results of other workers show some confusion, the present results as shown in diagram 11 show a very clear trend of decreasing K/Rb ratio as the rock type changes from tonalite to granodiorite to adamellite to granite. While Ahrens' limits of scatter apparently hold for most rock types a modification of the trend for acid intrusive rocks appears to be required, showing a more or less steady enrichment of rubidium with respect to potassium and apparently as the result of fractionation.

Different "magmas" may well start with different initial concentrations of rubidium and therefore cause similar rock types to fall on different parts of the graph thus accounting for some overlap of the already reported results. All these results do however, show the same trend, and more important, the effect of fractionation appears to change the K/Rb ratio significantly at a much earlier stage than the pegmatite fraction as originally shown by Taylor and Heier (1958).

The second half of diagram 11 shows a plot of log ppm rubidium versus log percent potassium for biotite. As might be expected the potassium concentration stays more or less constant but showing random variations, not only due to analytical errors, but also due to alteration of biotite to chlorite which causes a drop in the potassium concentration. The diagram also shows a progressive enrichment of rubidium as the host rock changes from granodiorite to granite, again indicating progressive fractionation.

Strontium

Diagram 13 shows the strontium concentration in feldspars and biotites and from these analyses it can be seen that strontium in the Cornwall and Weardale granites is practically an order of magnitude lower than for all the other granites analysed, a truly significant difference. As indicated by other analyses the Shap granite is practically intermediate between these two groups. Diagram 22 shows the strontium concentration in muscovite

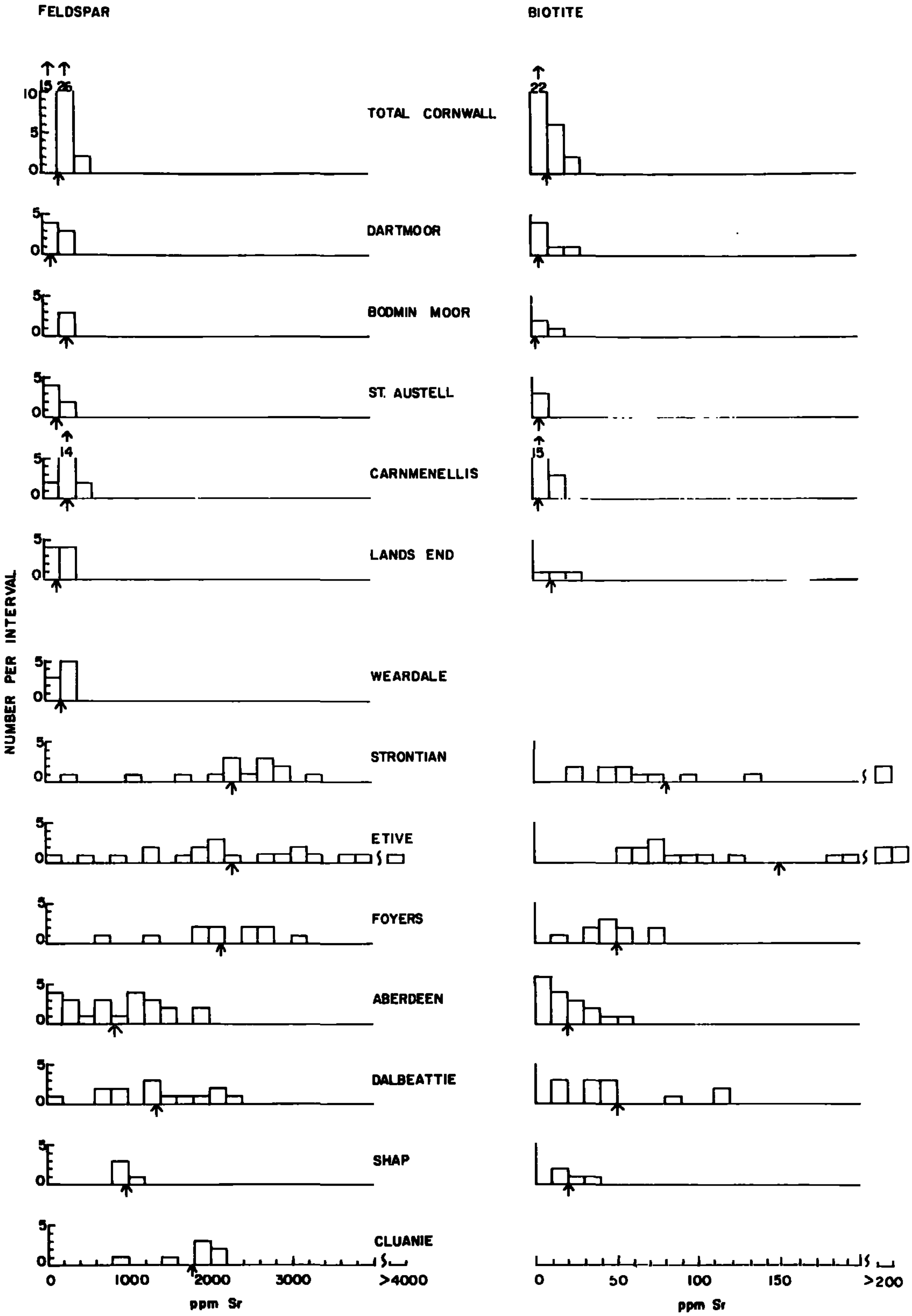

DIAGRAM 13 Sr ANALYSES

from Cornwall and Weardale to be almost the same. These analyses parallel similar observations made by Sen et al. (op.cit) and Wager and Mitchell (op.cit.) who found that the strontiun concentration declined with increased fractionation. This indicates that the Cornwall and Weardale granites are probably more highly fractionated than other granites.

Ca/Sr ratio in feldspars

Turekain and Kulp (1956), demonstrated a direct correlation between strontium and calcium concentrations in granites with analyses from 6 different stocks. They also found that as fractionation continued (i.e. as both the calcium and strontium concentration declined) the Ca/Sr ratio increased. Heier and Taylor (1959b), studying feldspars from Pre-Cambrian rocks of Norway, found a very similar Ca/Sr relationship, and explained this relationship by the fact that although calcium is smaller the bond strength of strontium is greater and will therefore obtain crystal sites more easily, leaving the last fraction relatively enriched in Calcium. Using the same samples as in their earlier paper (Taylor and Heier, 1958), they found that the rocks rich in rubidium were low in strontium (i.e. the pegmatites) and those low in rubidium were rich in strontium. It appears therefore, that exactly the same relationship exists between calcium and strontium as between rubidium and potassium but in reverse.

Diagram 14 shows a plot of log ppm strontium versus log percent calcium and exactly the same relationship is found as with the K/Rb plot, i.e. that the samples fall into three zones. Into the strontium poor zone fall the Cornwall and Weardale samples yet again indicating a high degree of fractionation. In the central normal area fall most of the other granites while in the strontium rich area there are the bulk of the Strontian and Cluanie samples and some of the Foyers and Etive samples. Therefore, as would be predicted, the Ca/Sr ratio reflects the K/Rb ratio and establishes the same information.

The strontium and rubidium concentrations and more particularly the

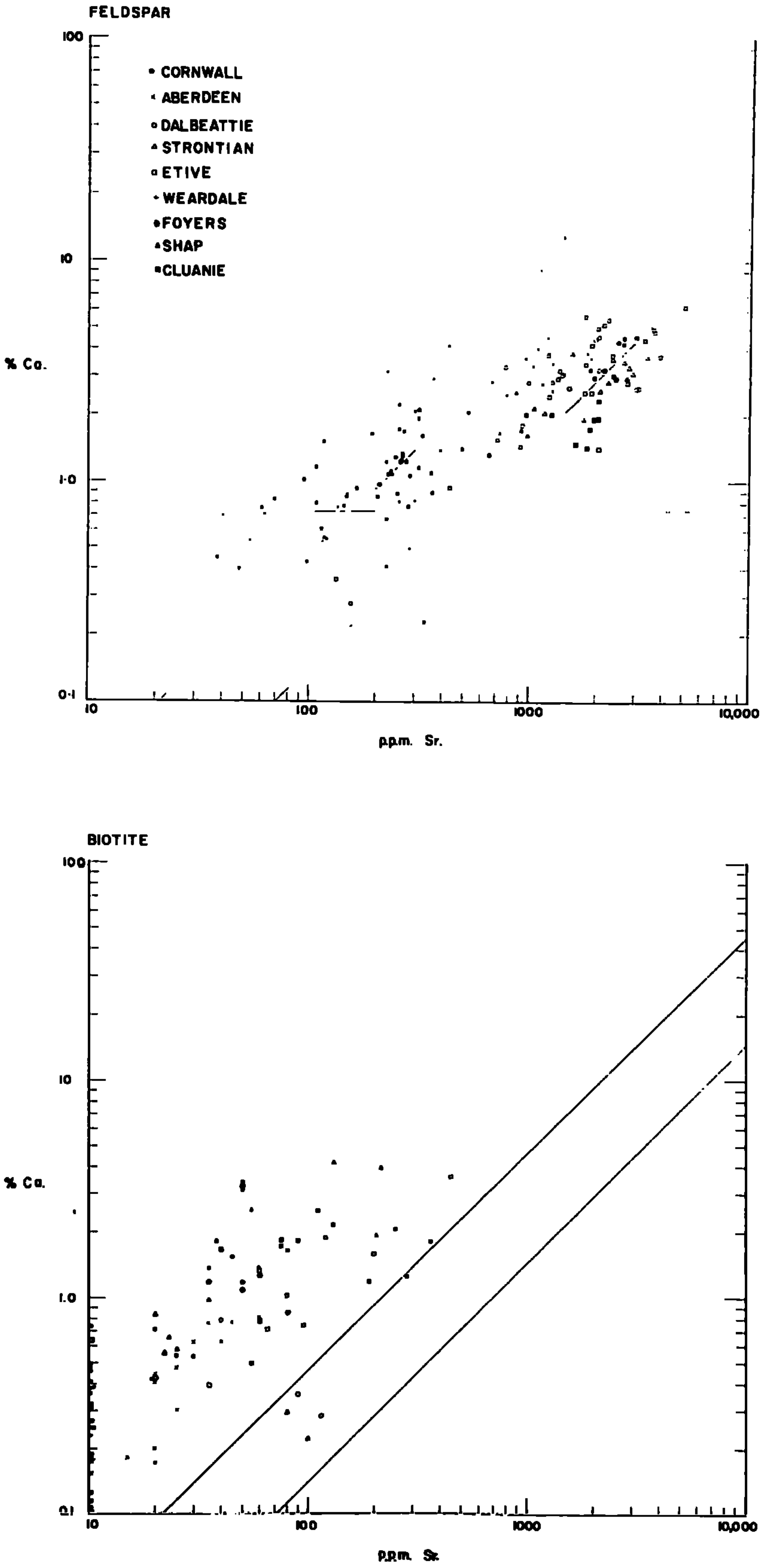

DIAGRAM 14 PLOTS OF Ca vs Sr IN FELDSPAR AND BIOTITE

smooth variation of the K/Rb and Sr/Ca ratios as found during fractionation of other rocks demonstrates quite clearly that all rocks tested have undergone some degree of fractionation. No assumption can be made to the composition of the original parent "magma" and there is nothing from the present analyses to indicate whether the parent "magma" was very much or only slightly more basic than the rocks presently observed.

On the basis of this information the interpretation of the heavy metal trace element analyses is made on the assumption that fractionation has been an active process. This interpretation is further confirmed by the presence of fractionation trends in individual stocks, particularly the St. Austell and Dalbeattie granites, as discussed later. No real estimate of the exact quantitative effect of fractionation on trace heavy metals can be made, but even in the case of pegmatites (see e.g. Heier and Taylor, 1958 and Wedepohl, 1956) the change from granite is generally only a factor of 2 to 4 for lead and a similar order of magnitude for other elements. It appears probable that with the change in rock types represented here the difference caused by fractionation is in the order of 10% to 100%. Whether a particular element shows an increase or decrease with fractionation has already been established by other workers and there appears to be no disagreement in the trends observed.

Lead

The histograms for lead are shown in diagrams 15 and 22 which also show the arithmetic mean. From these diagrams it can be seen that the average arithmetic mean of the feldspar analyses for the Cornwall area is 195 ppm, while those of St. Austell and Dartmoor are considerably lower. The other granites have a fairly constant average of about 105 ppm. These figures are in comparison with those given by Slawson et al. (1959) of 15 ppm, Wedepohl (1956) of 25 ppm and Heier and Taylor (1959a) of 15 and 26 ppm. These figures are for non-mineralised granites. For mineralised granites Slawson et al. give 50 ppm and Wedepohl 100 ppm; Wedepohl also gives an average of 100 ppm for pegmatites while Heier and Taylor, (1959a), give an average of 54 ppm for 30 Pre-Cambrian Norwegian pegmatites. It must also be remembered that in the absence of further

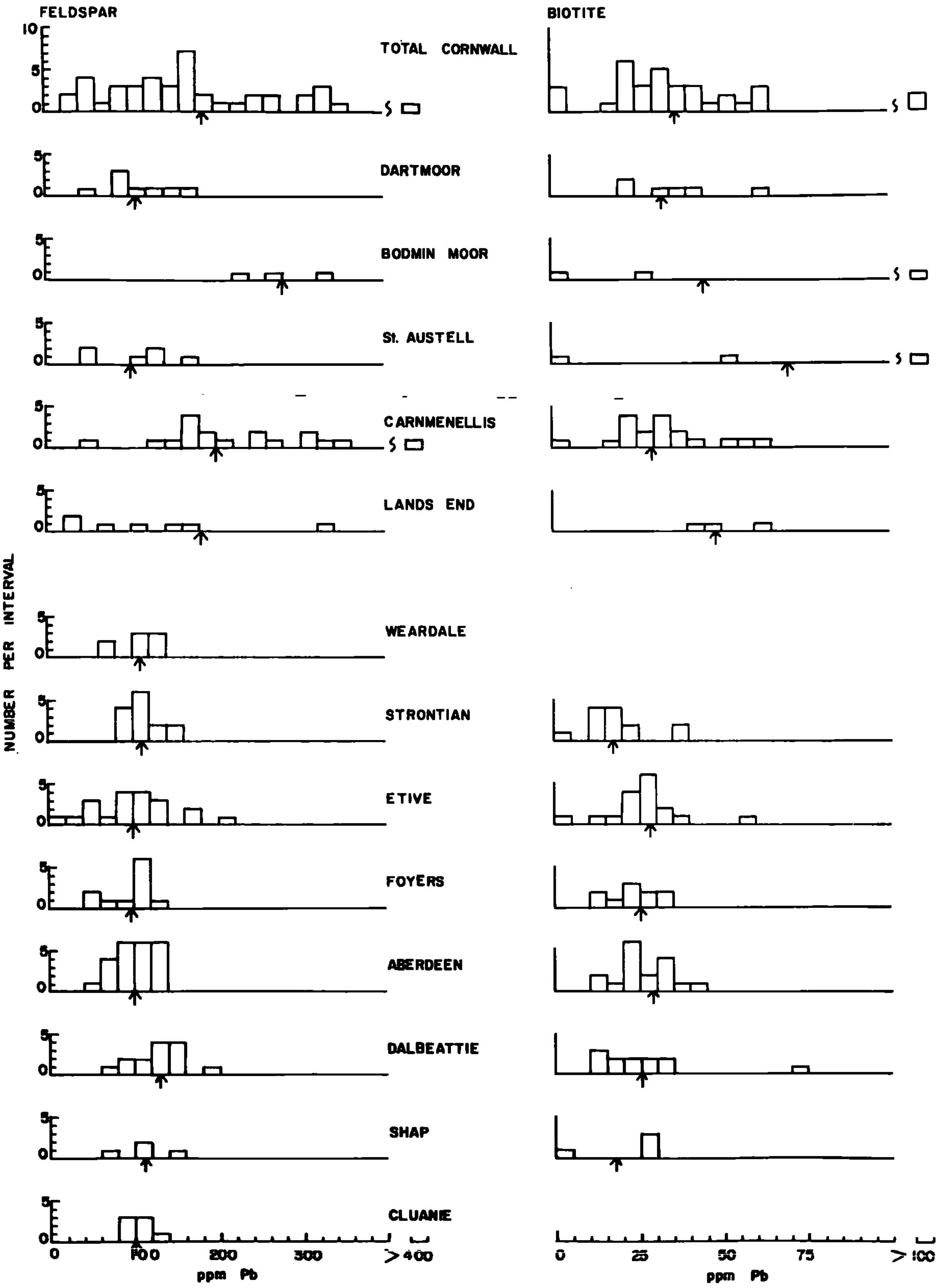

DIAGRAM 15 Pb ANALYSES

checks, as already discussed, all lead results may be as much as a factor of 2 too high but there can be little doubt that the present analyses are correct relative to one another.

The biotites from Cornwall average 38 ppm with variation between 31 ppm (Carnmenellis) and 69 ppm (St. Austell), the other granites being fairly uniform about 27 ppm with none higher than 29 ppm. These averages compare with 25 ppm quoted by Wedepohl (op.cit.) and 23 ppm quoted by Parry and Nackowski (1963) and averages of 14 to 20 ppm for 3 stocks given by Tauson et al. (1956) - all figures for non-mineralised granites. The only available data from a mineralised area is by Parry and Nackowski who quote 14 ppm for biotite from a quartz monzonite.

For muscovites (diagram 22) the average is 43 ppm for Cornwall and 16 ppm for the Weardale granite as compared with an average of 25 ppm given by Wedepohl for non-mineralised granites.

From an initial consideration it would appear that particularly for feldspars and muscovites there is, on the average, a significantly higher concentration of lead in the Cornwall samples than from all the others reflecting the presence mineralisation. However, there is yet to consider the added complication of the difference in the degree of fractionation between the Cornwall and Weardale samples as compared to the remainder. The average lead concentration in pegmatites has already been shown by other workers to run 2 to 4 times higher than for normal granites. This conclusion is further supported by the findings of Nockolds and Allen (1953), who state that in the rock series they studied the lead concentration increased as the rock became more fractionated. On the basis of these observations both the Cornwall and the Weardale granites should be higher in lead purely as a result of fractionation, but the Weardale granite although as highly fractionated as the Cornwall granites has quite a normal lead content with respect to other non-mineralised granites. It therefore appears probable that the high lead concentration in the Cornwall granite reflects only to a slight degree the effect of fractionation and in general it reflects the presence of lead mineralisation. It can be concluded therefore, that for the granites tested, high lead concentration in feldspar, biotite and especially muscovite, do indicate the probable proximity to mineralisation.

There has been some discussion in the literature concerning the geochemistry of lead. Sandell and Goldich (1943) analysed lead in several different rock types ranging in composition from gabbro to granite and showed a fairly close association between lead and potassium, i.e. as potassium increased lead also increased. They explained this by the similar ionic radii of K^{+1} (1.33Å) and Pb^{+2} (1.32Å). However, several workers, e.g. Slawson and Nackowski (1959) and Tauson and Kravchenko (1956) point out that the difference in charge will make direct substitution difficult. While a lead-feldspar ($PbAl_2Si_2O_8$) with a structure similar to orthoclase is thermodynamically stable (Rankama and Sahama, 1950), in order to equalise the electrovalent charge for each Pb^{+2} capture, an Al^{+3} ion must be admitted in place of a Si^{+4} ion according to the equation:-

$$KAlSi_3O_8 + Pb^{+2} + Al^{+3} = PbAl_2Si_2O_8 + K^{+1} + Si^{+4}$$

Tauson and Kravchenko also found that the lead concentration in plagioclase was as high as in orthoclase thereby indicating that there is no preferential isomorphism with K^{+1}. They also point out that the K/Rb ratio in biotite is completely different.

It would appear that Sandell and Goldich observed not necessarily a close agreement between potassium and lead, but simply that both potassium and lead increase by about the same amount during fractionation. They themselves point out that a similar close agreement was found between lead and silicon which could only represent a similar diffraction trend rather than a close geochemical association.

The Pb/K ratios determined during this present work are plotted on diagram 16. For the non-mineralised granites there is no real relationship between the lead and the potassium values, but for the mineralised Cornwall granites a definite correlation can be seen. It appears from this information that while the lead concentration is low (about its normal level for non-mineralised rocks) a significant amount of lead can substitute or absorb onto the surface of a crystal into a relatively large number of sites. When the concentration goes up the number of sites other than

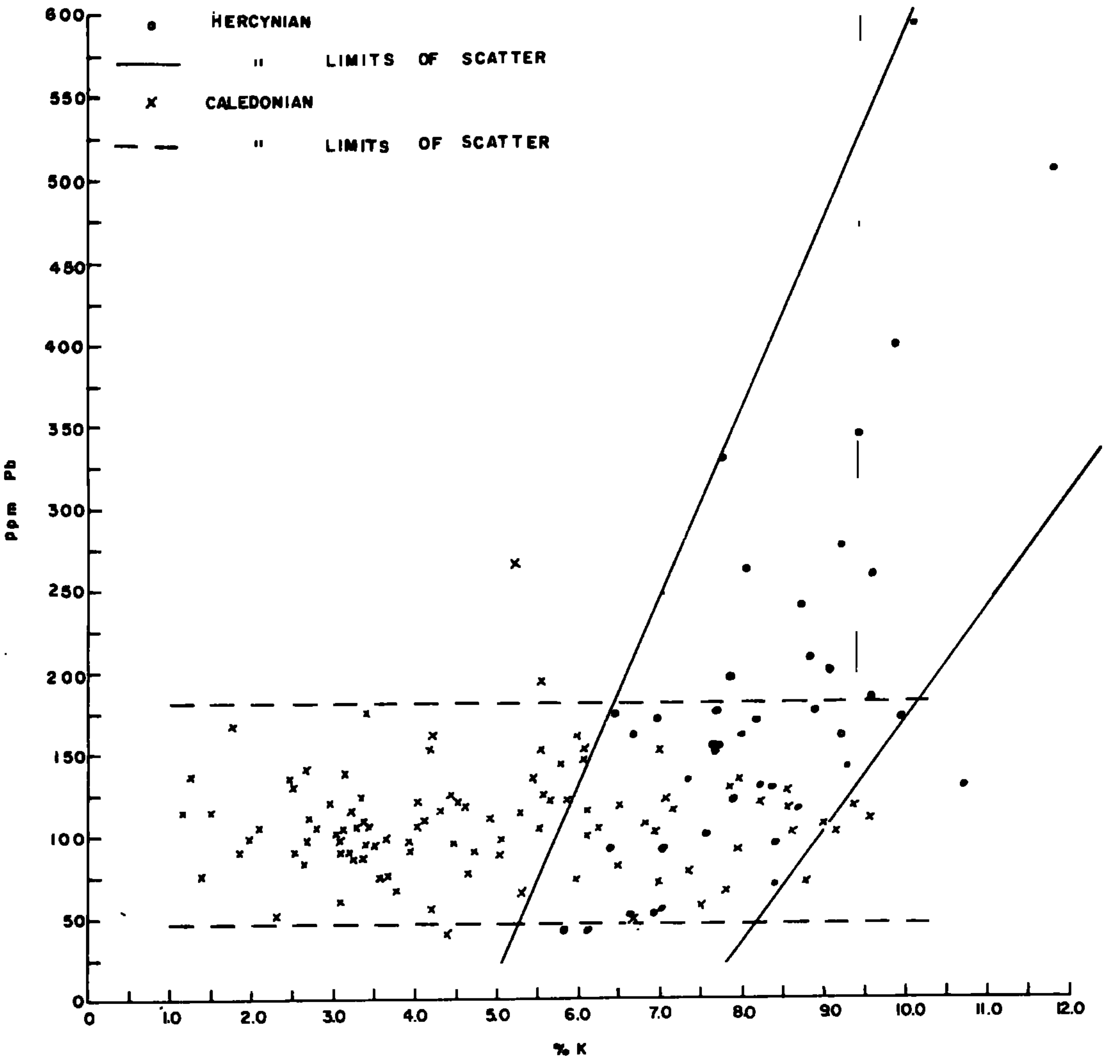

DIAGRAM 16 PLOTS OF Pb vs K IN FELDSPAR

potassium does not increase and it is only above this range that lead shows a correlation with potassium. On the other hand the Pb/K ratio in biotite shows no such relationship, even for the Cornwall granites. This probably reflects the different structure of the biotite and in particular the higher co-ordination number of potassium in biotite.

Copper

The average copper content of the feldspars from Cornwall is 37 ppm which coincides with the averages for the other granites which range between 25 and 45 ppm and shows no significant difference between them (diagram 17); only the Lands End granite with an average of 62 ppm falls outside this range. There are no figures available for the copper concentration in feldspars but Turekain and Wedepohl (1961), quote an average for non-mineralised low calcium granites of 30 ppm copper.

In biotite the average for Devon and Cornwall was found to be 36 ppm with variations from 21 to 50 ppm while the other granites were only slightly lower with averages varying between 24 and 40 ppm, again showing no significant difference. In general therefore, the two areas are indistinguishable on the basis of copper concentration in biotite. Parry and Nackowski (op.cit.) analysed biotite from quartz monzonite of the Basin and Range province and found an average of 29 ppm for non-mineralised and 1145 ppm for mineralised stocks.

The average for the Cornwall area muscovites is 59 ppm (diagram 22) but the variation about this mean is considerable. The Weardale granite has slightly less variation with an average of 22 ppm. There are no published analyses for comparison.

Although the information is not very complete for the very acid end of the scale, Wager and Mitchell (1951), have shown that copper is low in the early differentiates, at its maximum in intermediate rocks and drops off again for acid rocks. It is possible that fractionation has played a part in causing the Cornwall samples to have a lower copper concentration than they would have had they been less highly fractionated. Although the effect of fractionation cannot at present be separated from

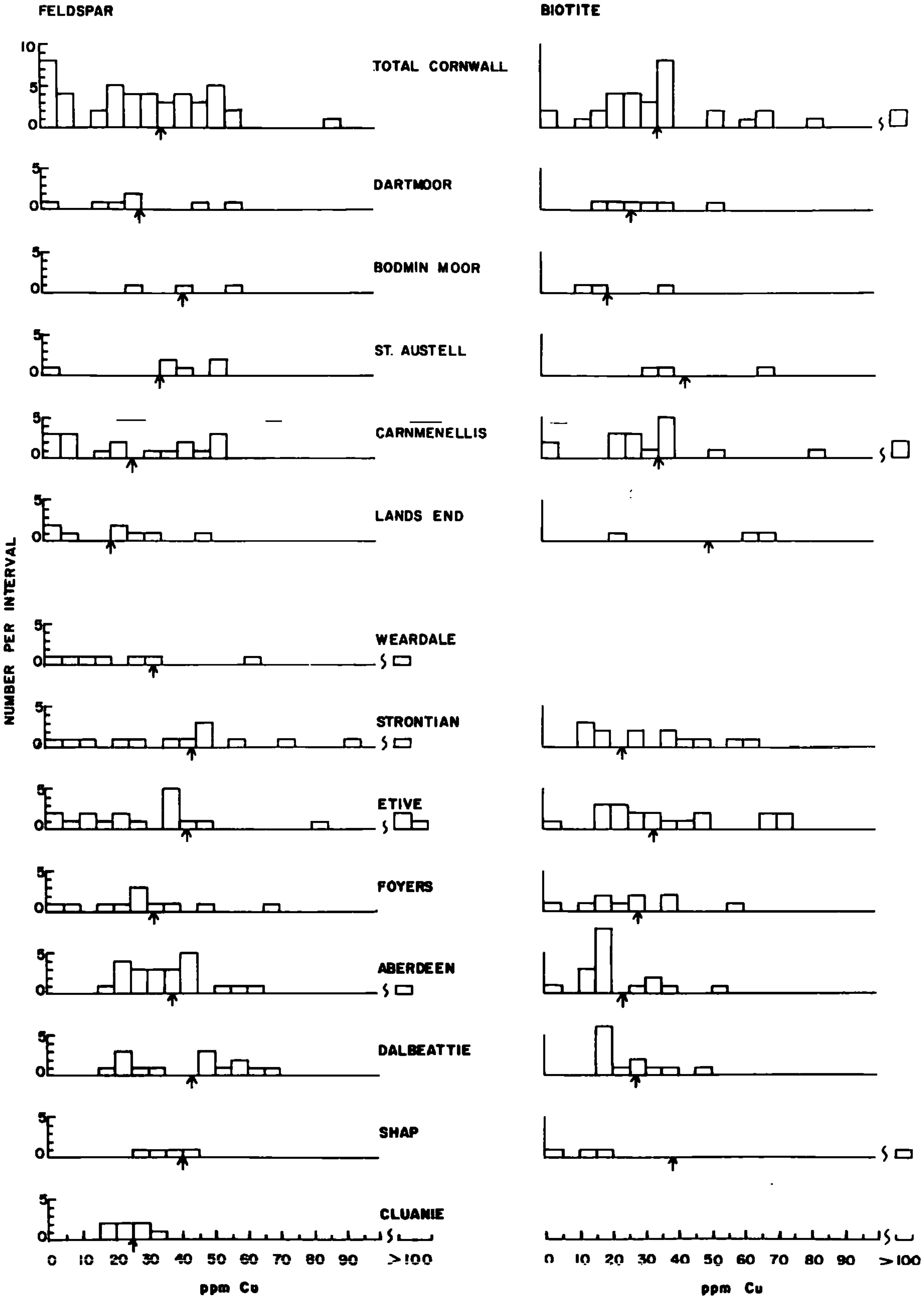

DIAGRAM 17 Cu ANALYSES

other variables it can be seen that the final result is that copper is of no use as a guide for mineral exploration in this particular area.

Zinc

The average zinc content of the feldspars from Devon and Cornwall is 28 ppm (diagram 18) with little variation about this mean except for Lands End which has an average of 62 ppm. The means of the other granites tested falls within the limits 0 ppm (Weardale) to 15 ppm (Shap) showing a significant difference from the Cornwall samples. These figures compare with a range of 5 to 15 ppm for feldspars from different non-mineralised granites as reported by Wedepohl (1953) and 10 to 24 ppm as reported by Tauson et al. (1956). There are no available figures for comparison with mineralised granite, but in general the zinc concentration in feldspar is low because most of zinc goes into ferromagnesian minerals.

As expected the zinc concentration in biotites is considerably higher than for feldspars, the average for Cornwall being 456 ppm with a low of 227 ppm (Lands End) and a high of 657 ppm (Bodmin Moor). On the other hand the averages for the other granites studied are quite uniform at about 350 ppm and show no significant difference from the Cornwall granites. The reported average values for the other non-mineralised granites show considerable variation, e.g. Wedepohl (op.cit.) reports an average of 380 ppm while Zlobin and Gorshkova (1961) report 220 ppm, Parry and Nackowski (op.cit.) 387 ppm, and Tauson et al. (1956), 620, 740 and 870 ppm from 3 different stocks. The only data available for mineralised granites is from Parry and Nackowski whose reported value of 287 ppm is lower than that for non-mineralised granites.

The arithmetic mean of zinc values for muscovite from Cornwall is 139 ppm with considerable variation about this mean, while the average for Weardale is considerably higher at 254 ppm. Both these figures are much higher than the reported value of 11 ppm for non-mineralised granites given by Wedepohl (1953).

With the exception of the muscovite results, the zinc concentration reflects the proximity to zinc mineralisation quite closely, but there is still the effect of fractionation to consider which is best carried out

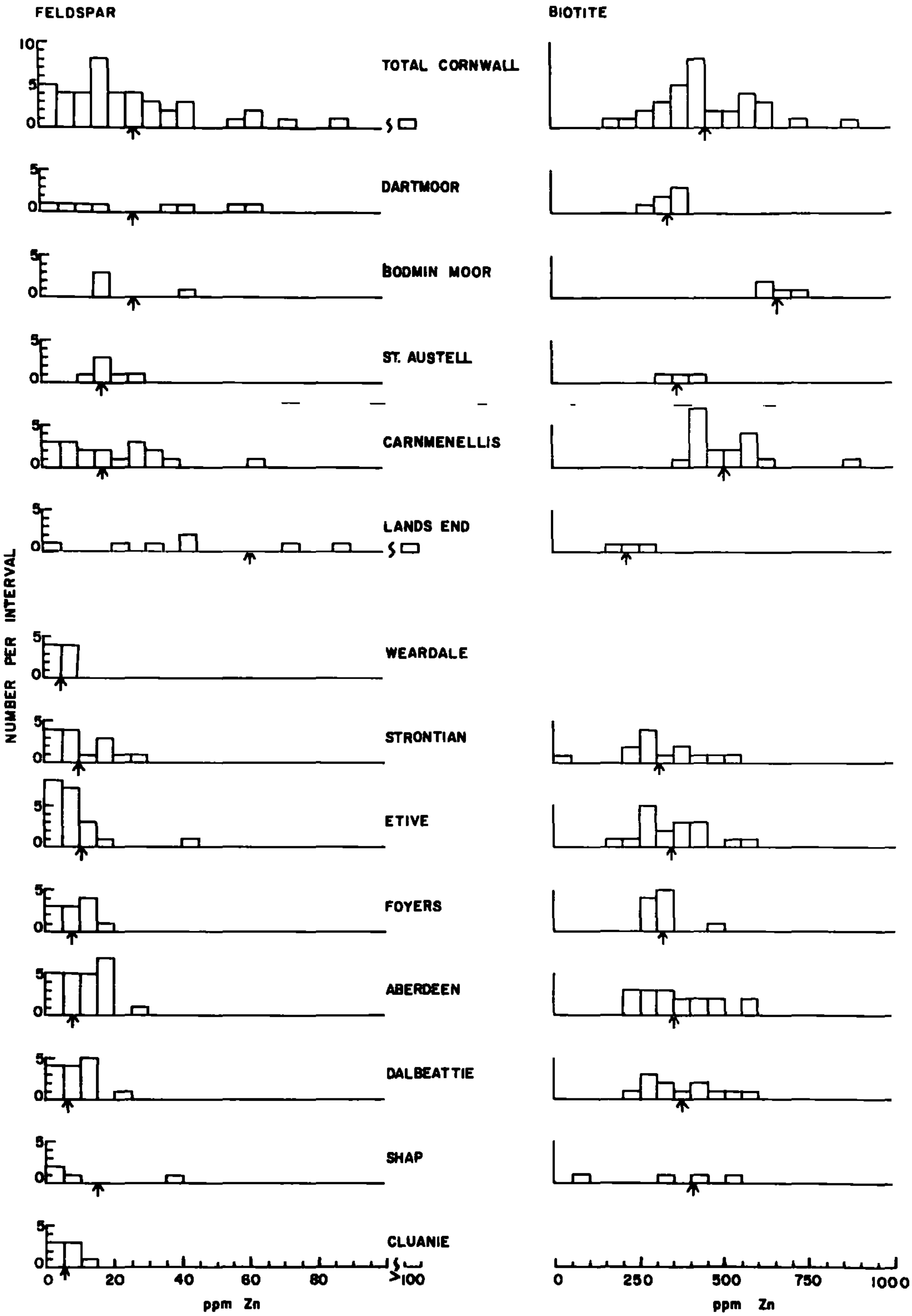

DIAGRAM 18 Zn ANALYSES

in conjunction with the manganese results and so will be discussed in the next section.

Zn/Mn ratio in biotites

During fractionation the zinc content tends to diminish as shown by Wedepohl's results (1953) where he quotes zinc in biotite from granite as having 11 ppm and zinc from pegmatites as 2 and 8.5 ppm. However, as indicated by the work of Sandell and Goldich (1943), particularly for biotites, the Zn/Mn ratio tends to remain constant. Diagram 19 is a histogram of the manganese analyses and diagram 20 a plot of manganese versus zinc in biotites and shows that all samples analysed fall within fairly narrow limits with the exception of the Cornwall samples which not only show a considerable scatter but also many fall in a zinc poor area although they have comparatively more manganese. Coupled with the fact that zinc concentrations have been found by other workers to diminish with fractionation, this indicates that there is an apparent <u>relative</u> reduction in the zinc concentration although the absolute amount of zinc is higher than for other areas. According therefore to the amount of fractionation which the Cornwall rocks have undergone, they should be lower in zinc than all the other granites with the exception of the Weardale granite. The fact that they are higher than these other granites indicates that the Cornwall samples are relatively much enriched in zinc, and they also, in this case, show a strong relationship to zinc mineralisation.

The zinc results for the feldspars were all too low to show any meaningful correlation and no strong correlation was found between manganese and zinc in the muscovites. The high zinc content of the Weardale granite muscovites with respect to those of Cornwall has no apparent explanation and appears to be purely a "reversal" of the type found by other workers, several examples of which have already been quoted.

Nickel

The nickel content of all feldspars is below the detectability limit

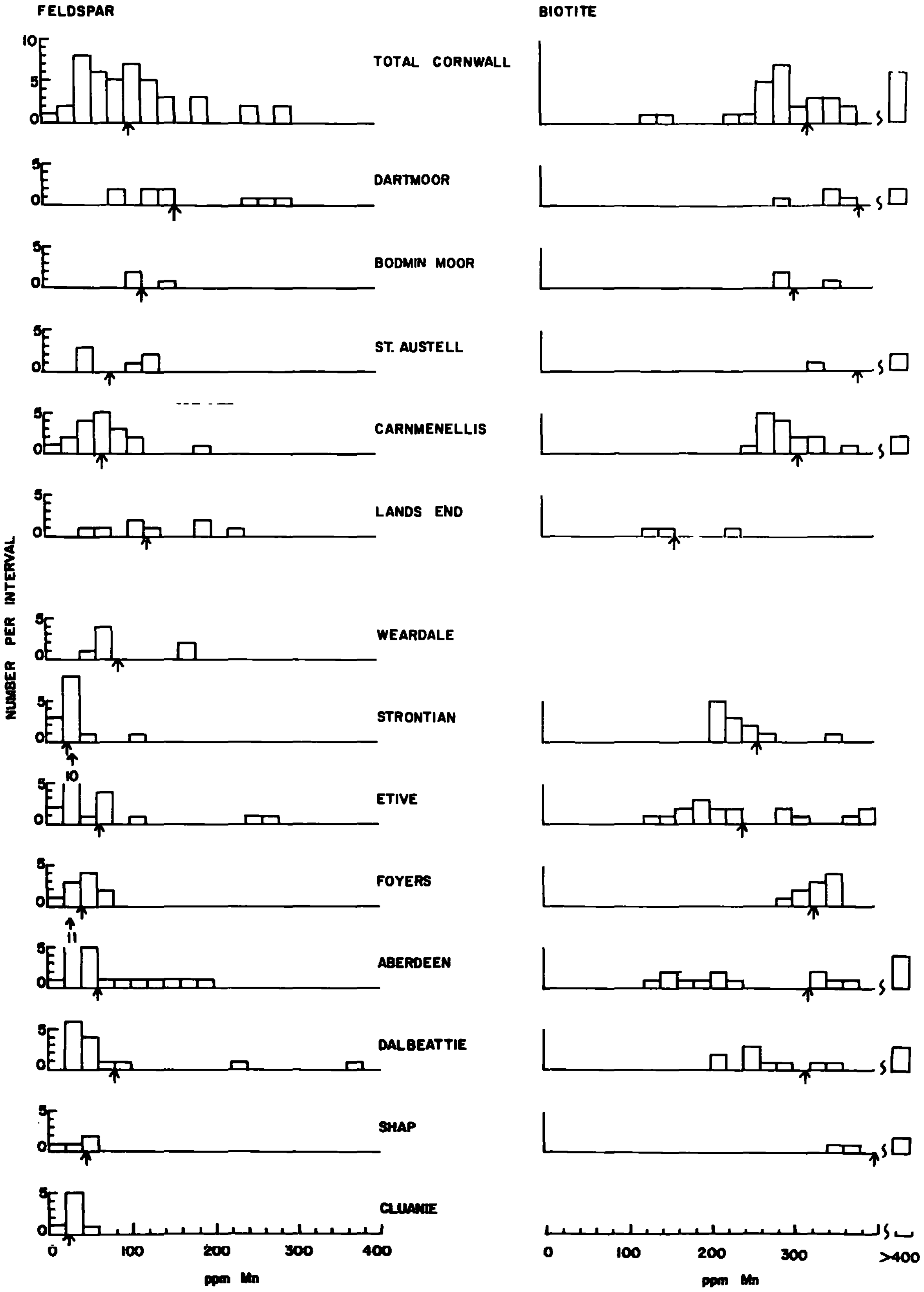

DIAGRAM 19 Mn ANALYSES

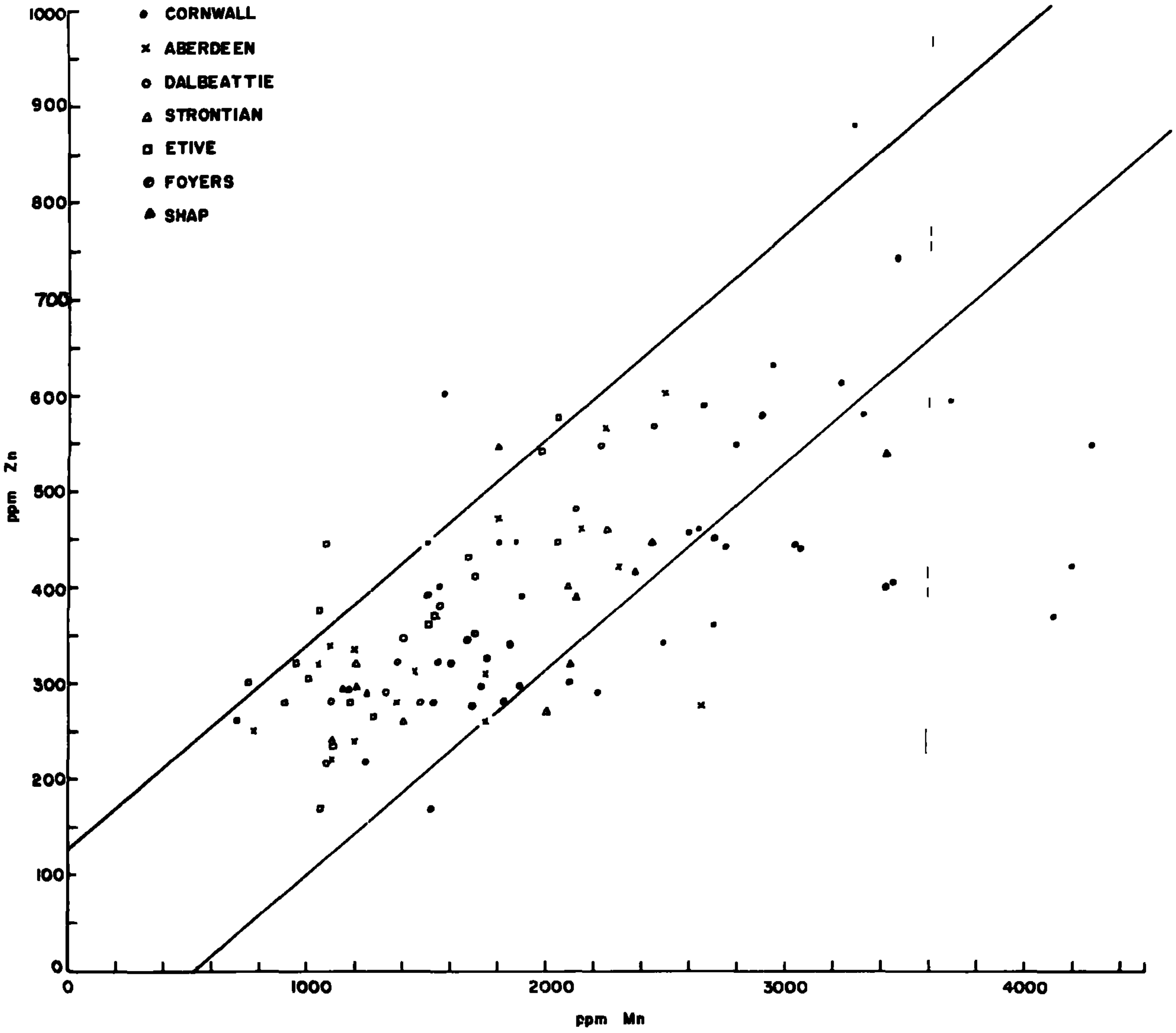

DIAGRAM 20 PLOTS OF Zn vs Mn IN BIOTITE

(8 ppm) in all cases.

For biotites (see diagram 21) the nickel content of the Cornwall stocks falls in the range 32 to 47 ppm with an average of 42 ppm, which is in contrast with the other granites, the lowest average for any being 50 ppm (Foyers), and in general the averages are much greater with Strontian (160 ppm) being the highest. There has been no indication of any nickel concentrations in the Cornwall area and in this respect there is no reason to suspect that they are any different from the other granites studied. The lower nickel values for the Cornwall granites probably simply represents the result of fractionation. Several workers, e.g. Wager and Mitchell (1951), Goldschmidt (1954), Sen et al. (1959) etc., have found that nickel decreases as fractionation increases and the present results fit well into these observations.

The very similar and low nickel concentrations in muscovite for both Cornwall and Weardale (26 and 18 ppm respectively) could well indicate the same degree of fractionation for both.

Zirconium

Zirconium was below the detectability limit (15 ppm) for all feldspars tested, but in biotite the average for Cornwall was 48 ppm (see diagram 21) with averages for the individual stocks varying between 30 and 117 ppm. The other granites were far more stable with variation between 54 and 86 ppm. Similarly the average for the Cornwall muscovites is very variable (between 0 and 77 ppm) with an overall average of 45 ppm while the Weardale granite has a more uniform distribution with 41 ppm.

The slightly lower average zirconium content for the Cornwall biotites most probably reflects the same degree of fractionation as already recorded. This would agree with data collected by Wager and Mitchell (1951) where they found that the very acid phases of the Skaergaard intrusion showed depletion in zirconium with respect to the earlier phases. The similarity in the Cornwall and Weardale muscovites indicates yet again that both have undergone a similar degree of fractionation.

Distribution of Element Populations

Several workers, e.g. Putman and Burnham (1963) and Warren and Delavault

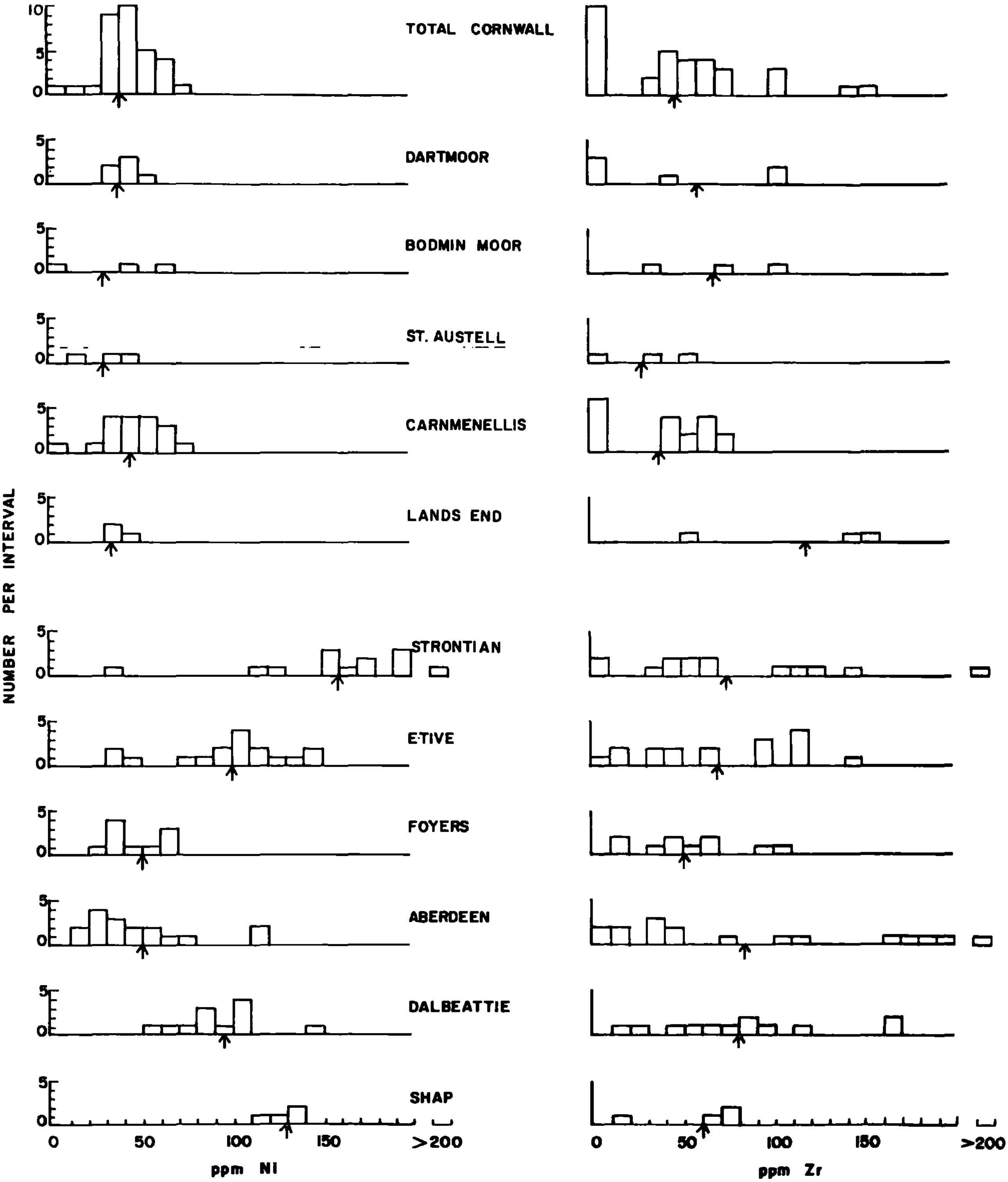

DIAGRAM 21 Ni AND Zr ANALYSES IN BIOTITE

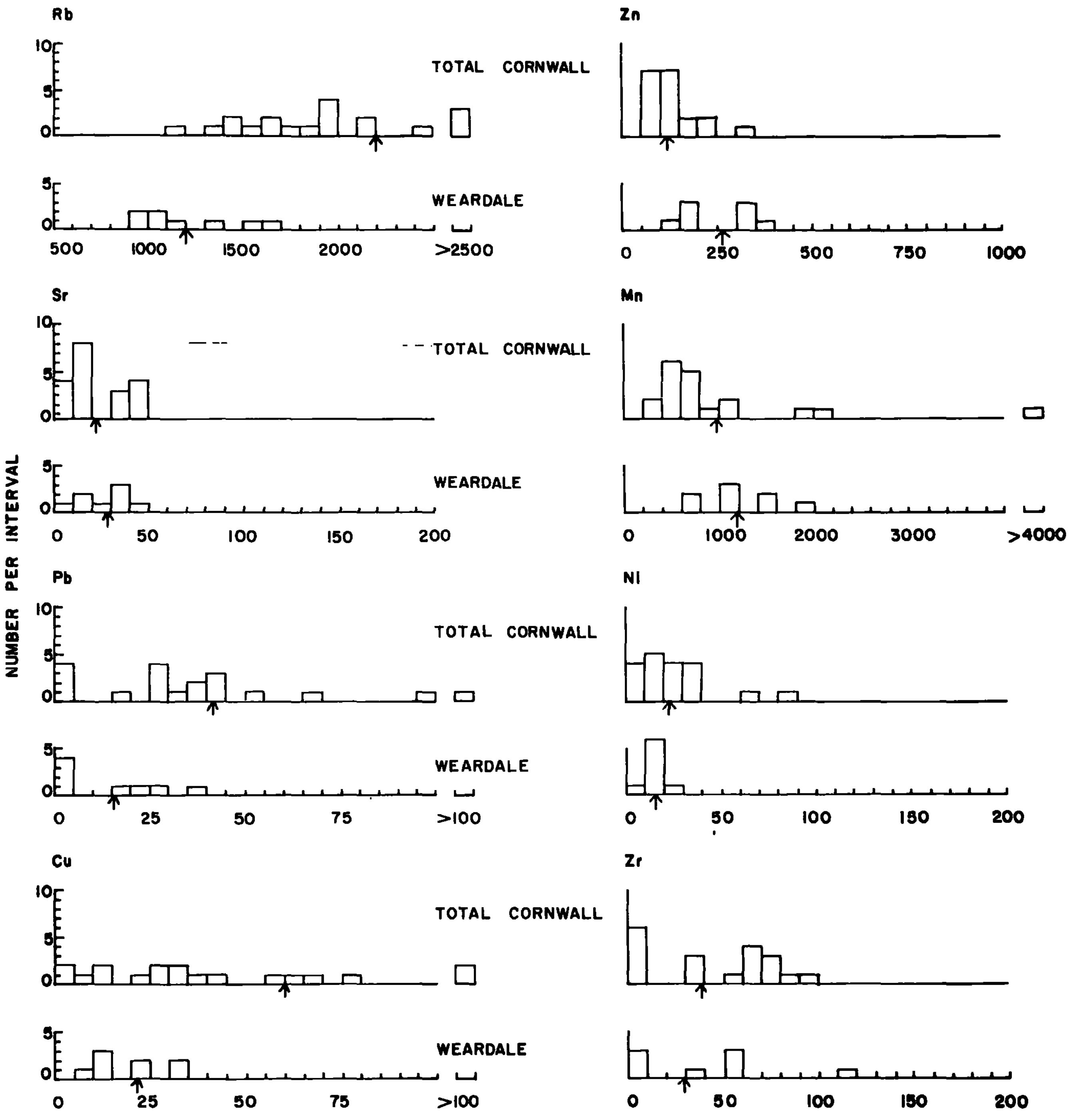

DIAGRAM 22 MUSCOVITE ANALYSES

(1960) etc., have come to the conclusion that each intrusive body has a unique trace element distribution which is different from other even associated plutons. If the plutons have more than one phase then it may or may not have more than one trace element population. This does not necessarily hold for every trace element compared between every pluton but it was reported to hold in the majority of cases.

It has already been shown in the present study that when treated as two groups the Cornwall and the Caledonian Scottish granites are distinctly different for almost every element tested, and if each group is now treated in detail the differences within each group are not so obvious, but nevertheless are still present. For example, choosing the Dartmoor granite, its strontium content is significantly different from the Bodmin Moor and Carnmenellis granites, its lead is different from the Bodmin Moor, Carnmenellis, Lands End and Cligga Head granites, its zinc different from the Lands End granite, manganese different from the St. Austell, Carnmenellis and Cligga Head granites, and copper different from the Lands End granite. That is, for the 6 trace elements tested the Dartmoor granite differs from all the other granites sampled in at least one trace element and generally more. The major elements show very much the same pattern. If the number of samples taken were larger so that a smaller difference in means could be detected then the Dartmoor granite would probably show even greater differences with respect to the other granites. Each granite if treated in this manner shows a very similar pattern to the Dartmoor granite, i.e. they all show significant variation for some elements compared to one another. These observations also indicate while the natural differences cannot be detected in every case the present sampling method of about 10 samples per granite is just sufficient to detect the natural variation between two associated granites and can more easily detect the difference between two non-associated granites.

Regional Studies

In each case only the geology and petrology as directly related to the geochemistry is discussed and no attempt is made to go into these in detail, rather the existing works have been relied on for this information and reference is given to them.

Devon and Cornwall

Dines (1956), gives a very detailed and complete list of all the mines and mineral production from this area, together with a short summary of the geology. The geology is further amplified by Bott et al. (1958), who discuss the magnetic and gravity data from this area, and by numerous other authors dealing with smaller aspects. Diagrams 8 to 22 include histograms of the total concentration of each element for each stock taken individually, but they do not include samples taken directly adjacent to mineralisation (i.e. the samples from Geevor Mine and Cligga Head) which are dealt with in a later section.

Mention has already been made of the element distribution in the Cornwall area as compared to the other granites and it has been shown that not only has there been considerably greater fractionation of the Cornwall rocks, but also that the high zinc and lead concentrations reflect the presence of zinc and lead mineralisation. Considering for the moment only the Devon and Cornwall area an attempt was made to find a uniform change in fractionation and/or a close correlation between lead and zinc concentration and mineral production. The histograms already mentioned show that there is an overlap of the concentration of some elements between stocks and no significant difference could be detected between these, although roughly 50% of the time a significant difference for one element compared between two stocks could be detected. Although the Cornwall area as a whole is far from homogeneous, as already shown by the large spread of results, one might expect, particularly bearing in mind the economic mineral zoning, a systematic change of the trace elements parallel to this zoning. No such pattern could be detected. Considering only the lead analyses a rough correlation was found between its concentration in feldspars and production, but in every other instance no such correlation was evident. It appears that a great deal more detailed work would be required to use primary cycle geochemistry for establishing the exact location of a mineral lode although the use of this type of survey on a regional scale i.e. for comparing the Cornwall mineralised and the Scottish non-mineralised granites, has already been demonstrated. No systematic pattern was detected in the major element distribution.

Lands End and Cligga Head

A total of 23 samples were analysed from the Lands End granite, 15 of these from Geevor Mine; the remaining 8 show normal variation and reflect a general uniformity over the area sampled. The one sample from the Cligga Head granite came from the exploration shaft which had been sunk in 1960. This granite outcrop is very small and heavily weathered on the surface, and as the exploration shaft was closed in 1962 only one fairly fresh sample from the dump was collected. This sample has obvious association with the mineralisation and is not discussed here.

Carnmenellis

The feldspar and biotite fractions from a total of 18 samples were analysed from the Carnmenellis granite and their locations, together with an outline of the granite and the three zones established by Gosh (1934) on petrographic evidence, are given in diagram 23. While "Gosh zones" 1 and 2 are adequately sampled, because of the complete lack of exposure in zone 3 only one fresh sample was available. Diagram 24 is a histogram of the Carnemenellis granite showing the distribution of the elements between the 3 zones. Insufficient data was collected on the major elements of the biotites to make a plot meaningful, and nickel in the feldspar, and strontium in the biotites are omitted because both were always below the detectability limit. It can be seen that on the basis of the major and trace elements there is no significant difference between zones 1 and 2, similarly the Na/Ca and Na/Rb ratios and the %An in the feldspars show no division; there is insufficient data from zone 3 to allow comment. This conclusion is in agreement with 15 modal analyses carried out by Chayes (1955) on rocks from zones 1 and 2 when he was able to conclude that there was no significant difference between the two zones on that basis; and it also agrees with work of A.L. Roberts (Camborne School of Mines, personal communication) who carried out a similar geochemical survey on total rock.

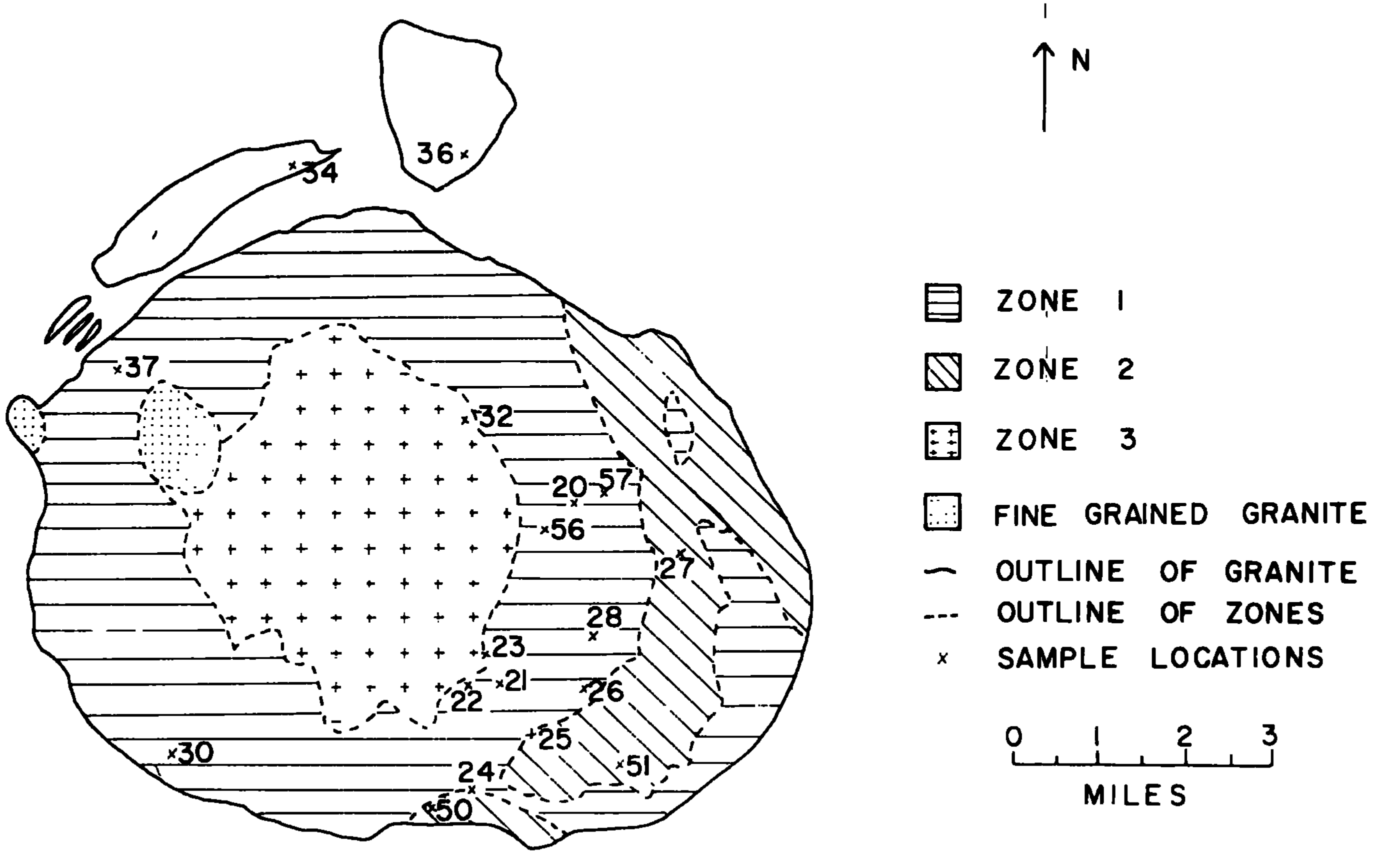

DIAGRAM 23 MAP OF THE CARNMENELLIS GRANITE AFTER GOSH (1934)

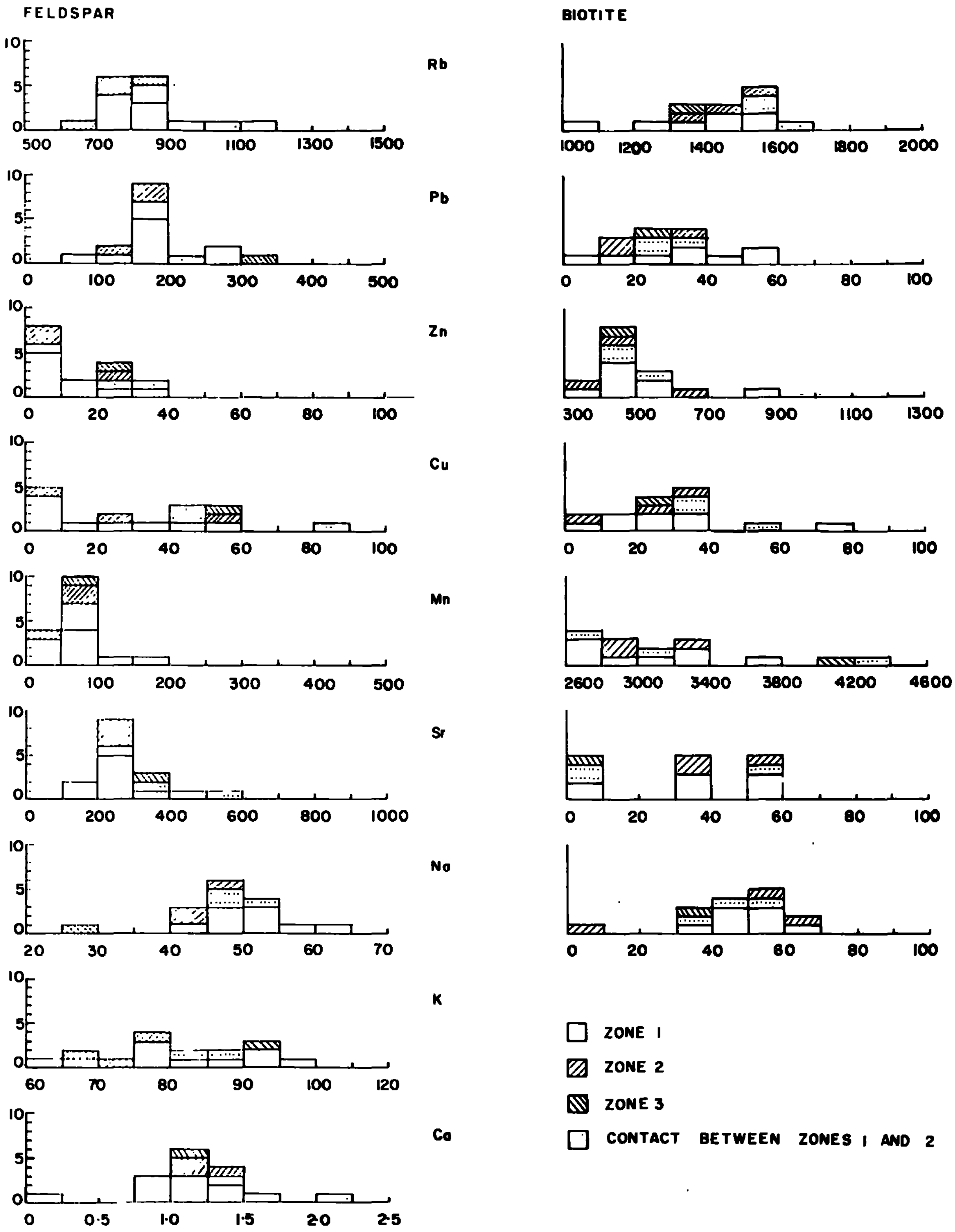

DIAGRAM 24 ANALYSES FROM THE CARNMENELLIS GRANITE

St. Austell

Six samples were analysed from the St. Austell granite, their location being shown in diagram 25 which also shows Exley's (1958) 4 different phases. The An composition, several mineral ratios, and the trace element concentrations of the feldspars from these different phases are given in table 13. It is evident from the element distribution that there is a significant difference between the 3 phases sampled, the %An, Na/Ca and K/Rb ratios in particular showing clear division. The strontium and lead concentrations generally reflect the 3 phases, while the zinc, copper and manganese results are random with respect to the 3 divisions. Sample C-54 appears to come from the region of the contact between phases 1 and 2, but, the presence of zinnwaldite (lithionite) and muscovite was confirmed on the separate micas by x-ray diffraction and the lithium concentration,determined using the optical spectrograph compared favourably with a standard zinnwaldite from the departmental collection (catalogue number 7806) and therefore this sample is placed in zone 2. The location of this sample near the contact may account for some of the slight differences it shows from the other sample in zone 2.

Bodmin Moor

The 3 samples analysed from Bodmin Moor granite all come from Gosh's "normal type granite" (Gosh, 1927) and are already shown in the histograms mentioned. They deserve no further special comment, except to point out that the trace element concentrations, Na/Ca and Rb/K ratios are fairly uniform.

Dartmoor

Eight samples were analysed from the Dartmoor granite, coming mostly from the Western side as this area afforded the best fresh exposure. With the exception of one or two quarries in operation the granite was deeply weathered everywhere. In the absence of more detailed petrological work than that given by Brammell and Harwood (1932) no further comment is possible.

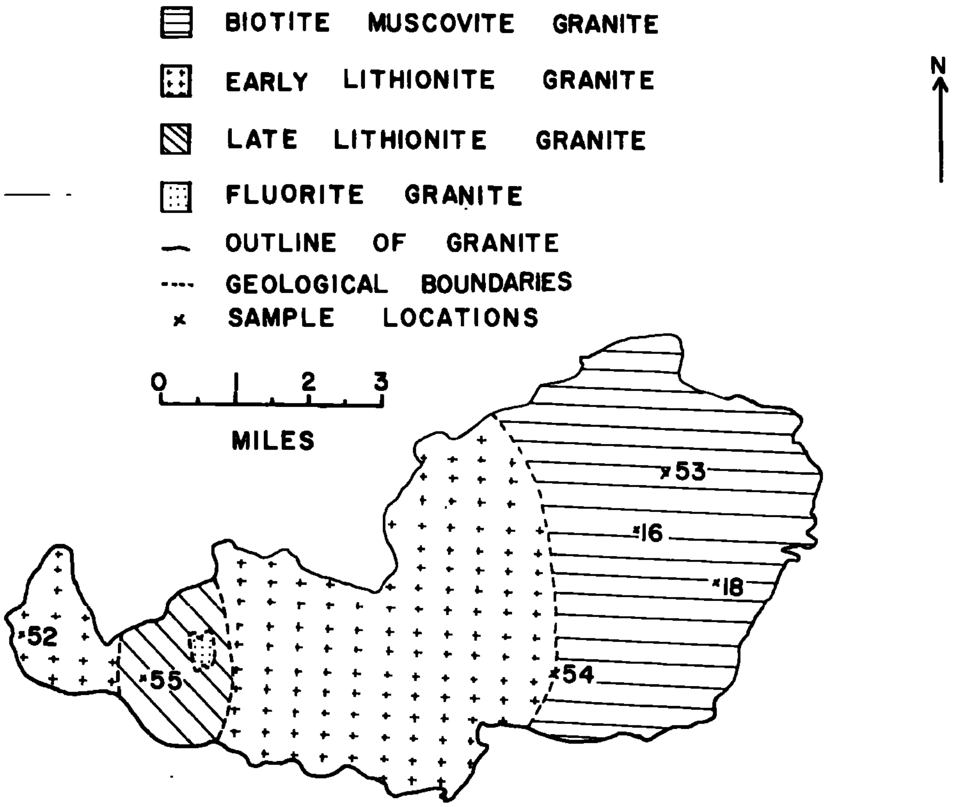

DIAGRAM 25 MAP OF THE St. AUSTELL GRANITE AFTER EXELY (1958)

Table 13

Major and Trace Element Analyses from the St.Austell Granite

Exley's granite types	Sample No	An (%)	Na/Ca	K/Rb	Sr ppm	Pb ppm	Zn ppm	Cu ppm	Mn ppm
1. Biotite muscovite granite (porphyritic)	C-16	23	3.54	125	117	128	15	52	130
	C-18	17	4.54	125	364	127	26	nd	45
	C-53	19	3.35	104	268	115	18	33	110
2. Early lithionite granite (porphyritic)	C-54	1 - 2	7.5	66	165	170	15	39	121
	C-52	1 - 2	7.13	132	61	41	21	35	50
3. Late lithionite granite	C-55	8	14.3	36	48	42	14	52	52

When treated in detail the petrology of the Devon and Cornwall granites is quite complicated and although the connection of the individual stocks to a common batholith has been established the granite can in no way be regarded as homogeneous. This makes exact comparison between stocks very difficult, but the use of geochemistry on a large scale in particular with reference to comparison with other granitic areas has been demonstrated. Far more detailed work is required on local geochemistry although certain applications, in particular as regards the St, Austell and Carnmenellis granites have been shown, and further detailed work on the Geevor Mine samples is to be discussed in a later section.

Weardale

The Weardale granite was sampled by using core from the Rookhope borehole (Dunham et al., 1965) and analysing 8 samples between 1,374' and 2,849'; the results are listed in appendix one. While the muscovite samples show a strong uniformity throughout, the feldspar samples show a considerable variation in copper and manganese analyses while the remainder of the elements are quite uniform as shown by the histograms. The uniformity indicates that, as found on petrological grounds, the Weardale granite is of the same type over the whole distance tested. Copper in particular, and manganese to some extent, shows a considerable variation for all granites tested and so these figures probably reflect only the geochemistry of copper and manganese rather than that of the granite.

Several small mineral veins have been found in the borehole, particularly fluorite, hematite and occasionally galena. Although several samples were taken from directly adjacent to the veins the influence from them could not be detected; e.g. sample W-1 and W-3 are about ¼ to ½" away from a fluorite vein with associated hematite, and sample W-6 is about 3" from a joint face showing galena. The veins are probably far too small to have had any significant influence on the surrounding rock, particularly bearing in mind the precision of the analyses.

As already discussed in the previous section the Weardale granite shows a much higher degree of fractionation than most normal granites, a fact which is reflected in the predominence of muscovite as the main ferro-magnesian mineral.

Shap

The shap quarry and small surrounding granite mass has been described by Granthum (1928), and more recently by Firman (1953). Although all four samples are taken from the same quarry there is considerable variation in the trace element content of both the feldspar and the biotite as shown by the histograms. This variation differs from the uniformity shown by the samples taken from the same quarry in the Carnmenellis granite (table 2) and probably not only reflects the coarse grained nature of the granite but also the very large number of accessory minerals and their random distribution as described by Granthum and Firman (op.cit.).

Criffell-Dalbeattie

The Criffell-Dalbeattie granodiorite has been studied most recently by Phillips (1956) who mapped, on the basis of petrographic evidence 4 main divisions; because of the basic nature of the rock and also because of the poor exposure only the 2 most acid phases, namely the granodiorite and porphyritic granodiorite are sampled. According to Phillips these last 2 phases were the result of forceful magmatic injection and subsequent cooling, the main granodiorite on the margin tending to become coarser grained towards the centre where it becomes porphyritic. The outline of the granite and other geological boundaries are shown in diagram 26 which also gives the sample locations. The mineralogy and petrology of the two main phases are very similar, and except for the increase in grain size and a decrease in hornblende concentration towards the centre of the body, there is little to distinguish between them. If this picture were correct, one would expect a general increase in the sodium and decrease in the calcium towards the centre, and also a decrease in the K/Rb ratio. Table 14 shows the concentration of the major elements and also the Na/Ca and K/Rb ratios. The figures in brackets in diagram 26 show the order of crystallisation based on the Na/Ca ratio and it can be seen, with few exceptions, that the Na/Ca ratio gets higher towards the centre, and again with few exceptions

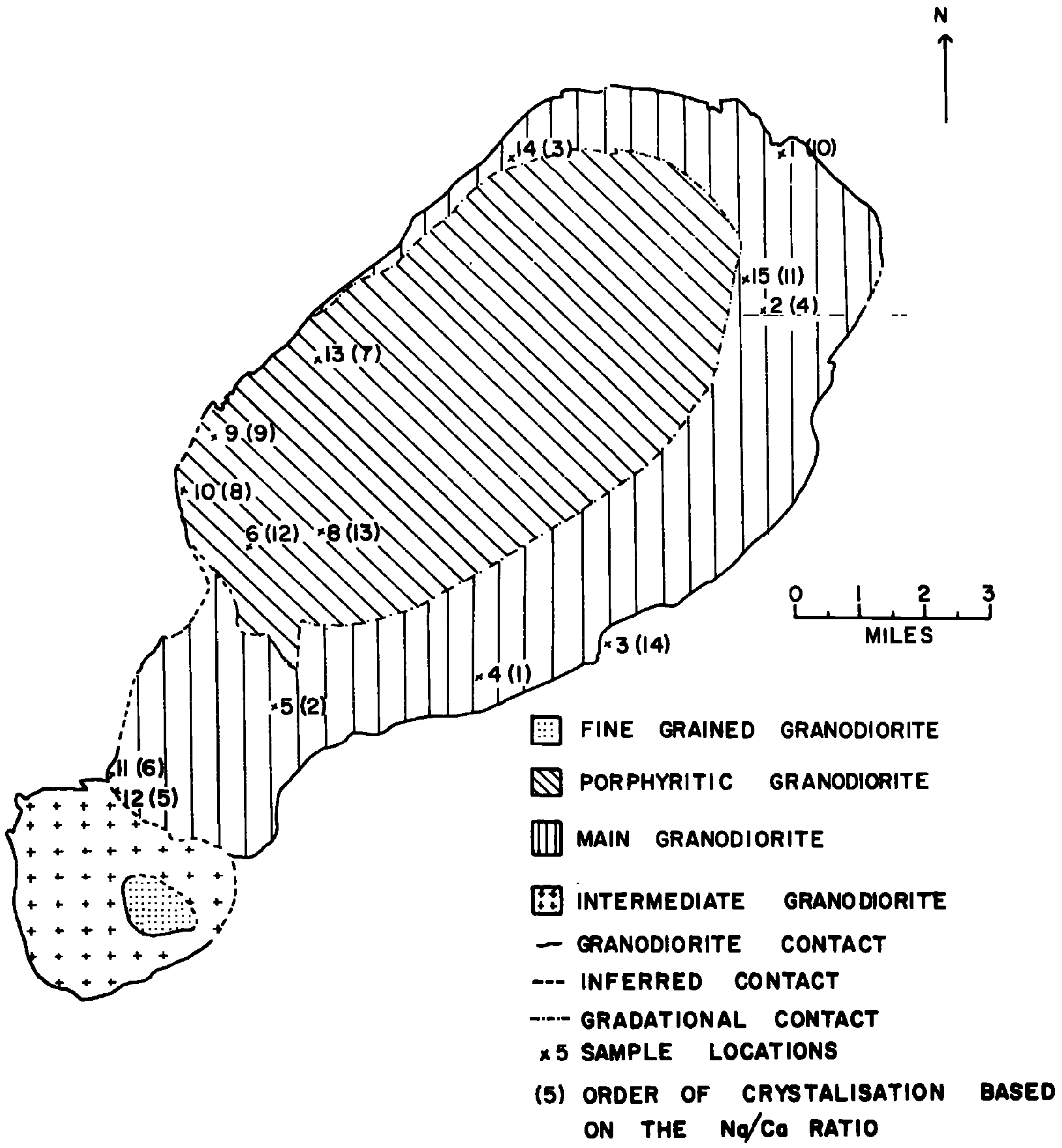

DIAGRAM 26 MAP OF THE CRIFFELL-DALBEATTIE GRANODIORITE AFTER PHILLIPS (1956)

Table 14

Major and Trace Element Analyses from the Criffell-Dalbeattie Granodiorite

	Main Granodiorite								Porphyritic Granodiorite					Aplite Dyke
	D-1	D-2	D-4	D-5	D-11	D-12	D-14	D-15	D-6	D-8	D-9	D-10	D-13	D-3
Na (%)	6.50	5.56	7.67	6.93	8.52	6.05	5.31	6.10	4.91	4.49	6.06	6.35	5.43	5.16
K (%)	3.94	4.17	4.39	4.41	2.45	5.64	3.22	5.53	6.88	7.12	6.06	5.46	5.51	3.75
Ca (%)	3.06	3.35	5.45	4.43	4.59	3.43	3.25	2.67	1.81	1.57	2.86	3.20	2.82	0.28
K/Rb	203	280	375	286	662	357	250	247	197	181	220	236	224	109
Na/Ca	2.12	1.66	1.41	1.57	1.86	1.76	1.63	2.28	2.71	2.86	2.12	1.98	1.93	18.43

this is reflected by a very similar order of crystallisation indicated by the K/Rb ratio. There are, however, three reversals which need explanation i.e. samples D-11 and D-12 on the western margin and D-1 on the eastern. D-11 and 12 were collected from a recent road cut on the very margin of the complex and it is possible that they represent the chill zone and therefore the average composition of the magma before diffraction started otherwise no ready explanation is found for the low calcium or high sodium content. Sample D-1 is also very close to the margin of the complex and in hand specimen shows quite considerable red alteration of the feldspars and as such differs from all other samples. The sample was taken from an old quarry and although the feldspars show no alteration to other minerals, it could be that the red "staining" has had significant effect on the chemical composition or that, like D-11 and 12 it reflects the average composition of the original magma, although in both cases no real chilled margin could be noted.

The trace element content of both the feldspar and biotite fractions shows no division between the two phases with the exception of the rubidium concentration of the feldspars which has already been shown by the K/Rb ratio. The smooth variation of the Na/Ca (and K/Rb) ratio with no marked division between the two phases and also the similarity of the trace elements between both phases fits the general picture as postulated by Phillips (op.cit) of the two phases separating by more or less continuous diffraction from the same magma.

The aplite dyke sample D-3, as might be expected shows considerably more fractionation than even the central most sample of the complex. This dyke was cutting the country rock adjacent to the margin of the complex and is shown by Phillips to be a late phase.

The Etive granite Complex

This area includes not only the Etive complex itself but also rocks from the Ballachulish granite to the west and the "Allt na Lairige" granite to the south-east. The latter is a small stock, about 5 by 4 miles, and 10 miles from the Etive complex proper, but no reference was found to this granite by name. As it is drained by the Allt na Lairige and there has recently been constructed a dam of the same name it seemed appropriate to name the granite likewise. The general geology is described in a memoir by Bailey and Maufe (1916) which has recently been revised by Bailey (1960).

It was extremely fortunate that, during the time spent in the field, the North of Scotland Hydro-Electric Board was just completing its Cruachan power scheme and the greater part of the 10 miles of tunnels, dam site excavations, and large underground turbine house with the resultant fresh exposure were all available for inspection. Over half of the tunnels were in the Cruachan granite of the Etive complex with the remainder being in more basic country rock. The rock weathering on the surface was too deep to allow satisfactory sampling and as no other part of the Etive complex had fresh exposure only analyses from the Cruachan granite are available. The Allt na Lairige granite had had a dam and access road built about three years previously and the Forestry Commission were just completing several roads in the Ballachulish Forest so that in both these areas, limited but fresh exposure was available.

All the Allt na Lairige samples (listed in appendix one) are of grey porphyritic granite and their analyses indicate a general uniformity in spite of the coarse grained nature of the rock.

The 13 analyses from the Cruachan granite appear distinct from the Allt na Lairige and Ballachulish analyses but show a certain variability. This variability reflects that reported by Anderson (1937) who said "of the various units ... (the) Cruachan granite shows the greatest variability in composition", (p.514). As already shown in the section discussing element ratios the majority of the samples from the Cruachan granite fall in the rubidium poor part of the potassium-rubidium graph. The possible reasons for this have already been outlined, but it is still interesting to note that few samples from a large number of analyses reported by several workers fall in this range. While no genetic implications can be drawn other than the possibility of an originally potassium or plagioclase rich or rubidium poor magma, (both the potassium and plagioclase content of the samples tested appeared quite normal) it does appear that the Etive, and also the Foyers and Strontian granites which fall in the same part of the graph, are distinct from a very large number of other "average granites".

The four Ballachulish granite samples show a general uniformity that would indicate one, more or less uniform intrusion over the area sampled. The averages of the analyses are quite distinct from those of the Etive and Allt na Lairige stocks.

Strontian and Foyers

In his well known paper on the Great Glen fault, Kennedy (1946), came to the conclusion, based on structural and petrographic evidence, that the Strontian and Foyers granites had been one single body which was subsequently separated by the Great Glen fault. The sample locations together with an outline map of both granites and the boundaries of the different granite types is shown in diagram 27. The map of Strontian is taken from Sabine (1963), and of Foyers from Pochin Mould (1946), both these maps being more detailed than those given by Kennedy but in general agreeing with his work. On the basis of data recently available from several Hydro-Electric Board boreholes (samples F-4, 5 and 6) the eastern contact has been found to lie slightly to the east of the position originally determined by Pochin Mould, diagram 27 is amended accordingly.

As already noted, the Strontian, Foyers and Etive granites show a marked difference from a large number of "average" granites in that they are rubidium poor with respect to potassium; because of the reported rarity of this state it indicates that some connection may exist between these three granites. It is also interesting to note that their strontium concentration is similar and yet quite distinct from all the other granites studied. The similarity on chemical grounds however, appears to stop there. Table 15 shows the average of each element, and two element ratios, for each major division of the Foyers and Strontian granite. From an examination of this table it is evident that there is no real correlation between the two granites. Although the tonalite results in particular are not as uniform as the results from other granites, this is only to be expected from the foliated and coarse grained nature and also the "considerable variation in the proportions of the minerals present", as reported by

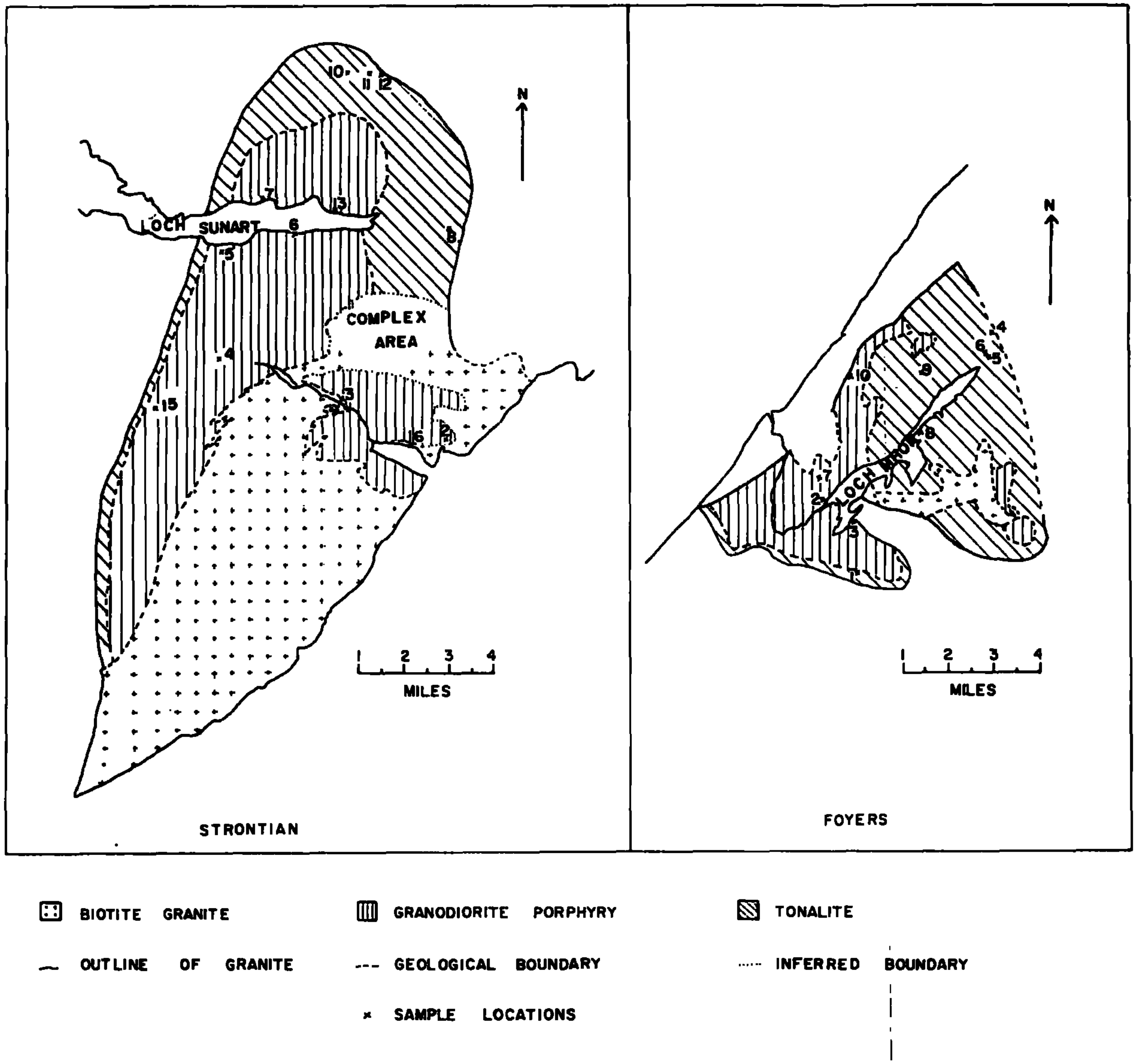

DIAGRAM 27 MAP OF THE STRONTIAN COMPLEX AFTER SABINE (1963) AND THE FOYERS COMPLEX AFTER POCHIN MOULD (1946).

Table 15

Analyses from the Foyers and Strontian Granites

Feldspar Fraction

Granite	Rock Type	Na/Ca	K/Rb	Na (%)	Ca (%)	K (%)	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Mn ppm	Cr ppm
Strontian	Tonalite	1.70	499	6.24	3.80	3.80	2102	75	121	8	62	40	46
	Granodiorite Porphyry	2.13	762	6.15	3.04	3.29	2533	60	105	11	39	25	23
	Biotite Granite	2.56	211	5.39	2.09	5.02	1165	237	89	nd	nd	27	20
Foyers	Tonalite	1.65	1150	5.21	2.14	5.17	2096	56	89	5	26	44	33
	Granodiorite Porphyry	1.66	973	5.55	3.38	4.49	2153	58	114	6	33	38	28

Biotite Fraction

Granite	Rock Type	Zr ppm	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Mn ppm	Ni ppm
Strontian	Tonalite	56	64	280	18	330	31	2678	138
	Granodiorite Porphyry	79	102	237	18	289	35	2310	179
	Biotite Granite	158	60	376	36	545	15	3500	130
Foyers	Tonalite	58	55	187	30	322	23	3408	43
	Granodiorite Porphyry	50	48	193	21	338	36	3225	60

Sabine (1963). In spite of this the tonalite analyses are still, in general, distinct from the analyses of other rock types. The porphyritic granodiorite shows greater uniformity but still exhibits some variation. In the histograms given in diagrams 8 to 22 it can be seen that for both the feldspar and biotite fractions the variation of the lead, copper, calcium, sodium and potassium contents between the two granites is as great as for completely unassociated granites, while for the biotite fraction alone the strontium and nickel contents also show a large variation. The rubidium results are all too low to have much significance and the zinc and manganese results appear similar for both granites. In his paper Kennedy (op.cit.) estimated that the vertical movement was probably not less than 6000' and not more than 3 to 4 miles. It is quite conceivable that vertical variation of this magnitude could cause differences in the chemical composition, but as the horizontal distances are greater than this in both granites, and as, generally speaking, variation at right angles to the contact can be expected to be greater than that parallel to, this factor is probably considerably smaller than the variation already described.

While both granites show obvious similarities Pochin Mould (op.cit.) outlines several petrological differences in her paper. In addition, from the present work it appears that there are no more than random chemical similarities, and on this basis it must be concluded that the Strontian and Foyers granites probably do not have any closer association than is shown by most of the other Caledonian granites; confirmation of this is found in histograms 8 to 22 which compare and contrast with all the granites studied.

Cluanie

The Cluanie granodiorite is about 3 miles by 2 miles and has recently been described by Leedal (1952) who found no variation of any significance within this stock and attributed its origin to magmatic injection. The results in appendix 1, and diagrams 8 to 22, show that the Cluanie granodiorite is the most uniform chemically of any granite tested, which indicates a magmatic origin (poor uniformity is no evidence of a non-magmatic origin) with (practically) no fractionation or assimilation of country rock. The analyses of the granite are not only useful for comparison with other granites, but also indicate the degree of uniformity that can be obtained and help emphasise the non-uniformity of other granites by establishing a basis for comparison.

Aberdeen Area

This area includes not only the Aberdeen granite (or the Hill of Fare granite as it is sometimes referred to) but also the Granton, Peterhead, Fraserburgh and Strathdearn (or Findhorn) granites. No attempt is made to go into the geochemistry in detail, partly because of the lack of recent descriptions of these granites (Bisset 1932 being the most recent published detailed description) and partly because of the large number of different granite types for which the 23 samples analysed are too few to allow detailed comment. The histograms (diagrams 8 to 22) show an amazing similarity between all the stocks, far more so than for many other apparently more homogeneous granites. The probable connection of some of the Aberdeen area granites to a common Batholith has already been discussed by Barrow and Craig (1912), and from a spatial relationship such a hypothesis would seem quite feasible. Considering the analyses tabulated here it would appear that the granites of this area have probably, in large part, been derived from the same rather homogeneous source even if they are not now directly connected to a common batholith. It would also indicate that the differences in colour and mineral composition have quite a small effect on the trace element and some of the major element contents, which are more homogeneous than for most suites of granite. Considerably more detailed work would be required to confirm a common batholith theory but the present preliminary observations indicate that it is a strong possibility.

Wall Rock Alteration

The origin of economic deposits has always been very much in dispute, and frequently the shape of dispersion pattern found can help in deciding this point. While the dispersion pattern itself be open to question as to its type, it is generally possible to tell at least the direction of movement of any ore forming fluids with respect to the wall rock. That is, whether

Diagram 28

Wall Rock dispersion patterns after Reitan, (1959)

Diagram A implies diffusion from concentration in the vein, into the country rock.

Diagram B implies "leakage" from the surrounding rock and concentration in the vein.

Diagram C implies movement from the vein into the surrounding rock, of surrouding rock material already low in the vein.

Diagram D implies that cations are residually enriched in the surroundin rock as other material moves into the vein.

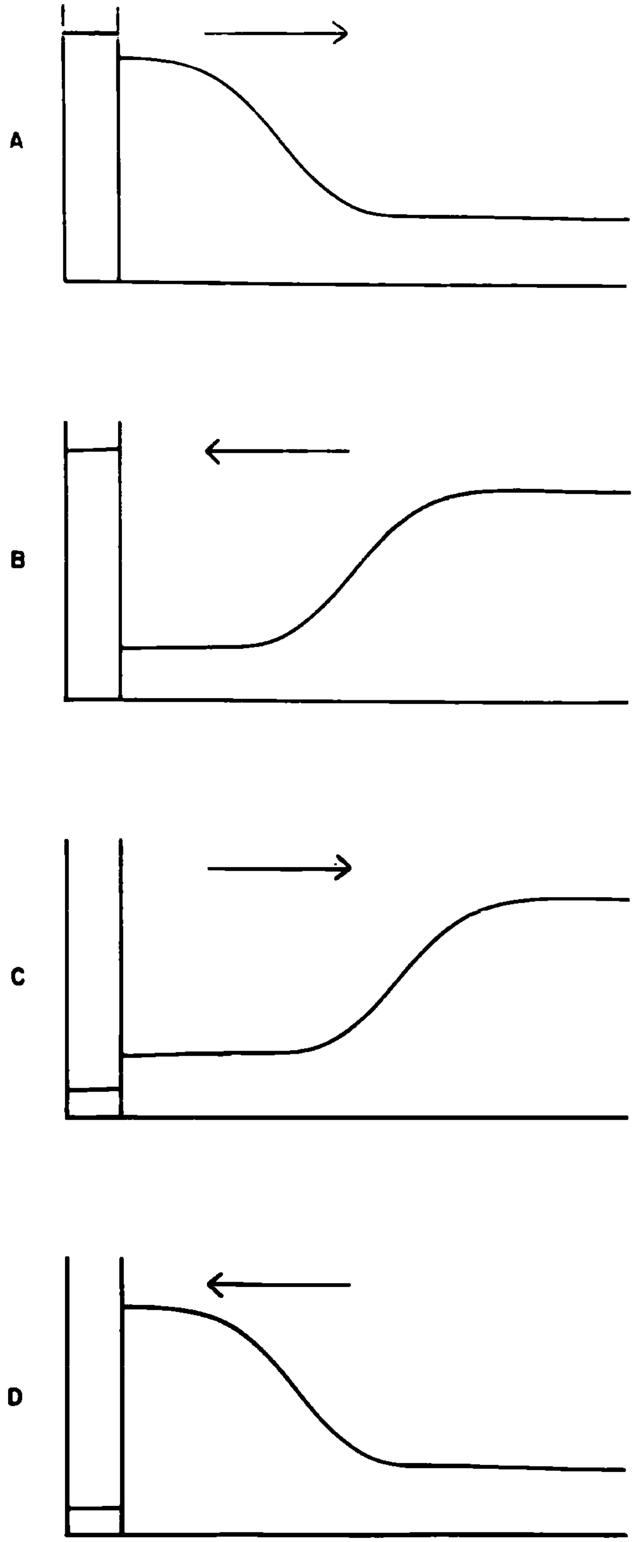

DIAGRAM 28 WALL ROCK DISPERSION PATTERNS AFTER REITAN (1959)

the economic minerals moved out of, or into, the wall rock. This question has been discussed by Reitan (1959) whose diagrams, with explanatory notes, are reproduced here, diagram 28 a-d.

Most of the examples quoted in the literature appear to be the type of dispersion pattern which would be expected from deposits with a hydrothermal origin, or any other origin which involves emplacement from the source into the host rock, (e.g. Morris and Lovering, 1952 and many others). Several examples of type b have been reported; e.g. Boyle (1963) summarises his arguments to prove diffusion of metals from the country rocks into the vein to form ore deposits, using as specific examples the Yellowknife gold mines, North West Territories, Kino Hill silver-lead-zinc deposits, North West Territories, and the Bathurst New Brunswick, lead-copper-zinc deposits. In all these areas he finds a dispersion of type b. Perhaps one of the most convincing arguments which he presents is the occurence of gold in ice lenses in the perma-frost layer at Yellowknife. Oftedal (1961), working on barium and strontium rich pegmatites in Norway, also reports a trace element distribution as shown in figure b.

As neither of the types of dispersion represented in figures c or d can produce economic mineral deposits, they are not considered further.

During the present study samples were taken at distances up to 350 feet from a working tin vein in Geevor Mine, Cornwall. The lode (PB4) was about 8 feet wide with fine grained disseminated cassiterite averaging about 75 pounds per ton, and minor associated chalcopyrite and pyrite. Close to the vein the feldspars were altered to a deep red and most of the ferromagnesian material had been removed. This alteration zone was about 7 feet wide on either side of the mineral vein and stopped abruptly; beyond this limit for all veins the granite appeared quite normal.
Mr. A.L. Roberts (Camborne School of Mines, personal communication) analysed total rock, feldspar and biotite for a distance of about 15 feet from one of the Geevor Mine tin veins (11W6) and found that all elements analysed (tin, zinc, beryllium and copper) were high in the alteration zone but dropped to normal as soon as the alteration zone ended. Rao (1952), also analysed total rock feldspar and biotite for a distance of 4 to 14 feet away from a tin lode in South Crofty Mine Cornwall for 17 different elements.

He reported an increase in tin, cobalt and manganese in the alteration zone and a decrease in rubidium, lithium, chromium, vanadium, nickel, barium, titanium, lead and strontium and practically no change for lanthanum and yttrium. He also found that there was not much change in the trace element concentration outside the red alteration zone.

In the present study a total of 15 samples were analysed in a single traverse along the cross-cut east of vein PB4. The traverse passed through 7 feet of red alteration zone from the edge of the mineral lode proper, then through 85 feet of unaltered granite, 4 feet of red alteration, 14 feet of unaltered granite, another 4 feet of red alteration and then to the end of the traverse (350 feet) in unaltered rock. The two small veins at 95 and 115 feet showed signs of mineralisation but were uneconomic for mining production. All samples had sufficient feldspar for analysis, but biotite was absent from the alteration zone and therefore the analysis for this mineral is not complete; care was taken to exclude any samples showing mineralisation. The change of the trace elements away from the mineral zone is shown in diagram 29 together with the average values for the Lands End granite (shown as a dotted line). The details of the distribution of each element is taken in turn.

Sodium, potassium and calcium

In the feldspar samples the potassium is enriched and the calcium and sodium are impoverished in the alteration zone, while all 3 remain more or less constant within the limits of the fresh granite. The sodium concentration drops to zero in the sample directly adjacent to the mineral vein while the calcium concentration drops very nearly to zero, this change reflects very closely the plagioclase concentration which is found to drop steadily in the alteration zone, disappearing altogether next to the mineral vein as shown by the modal values in appendix one. Conversely the potassium concentration rises sharply near the mineral vein as does the orthoclase content, probably as a result of residual enrichment following the removal of plagioclase and biotite.

Only potassium and calcium were determined in the biotite samples, and the concentration of biotite in the alteration zone was generally too

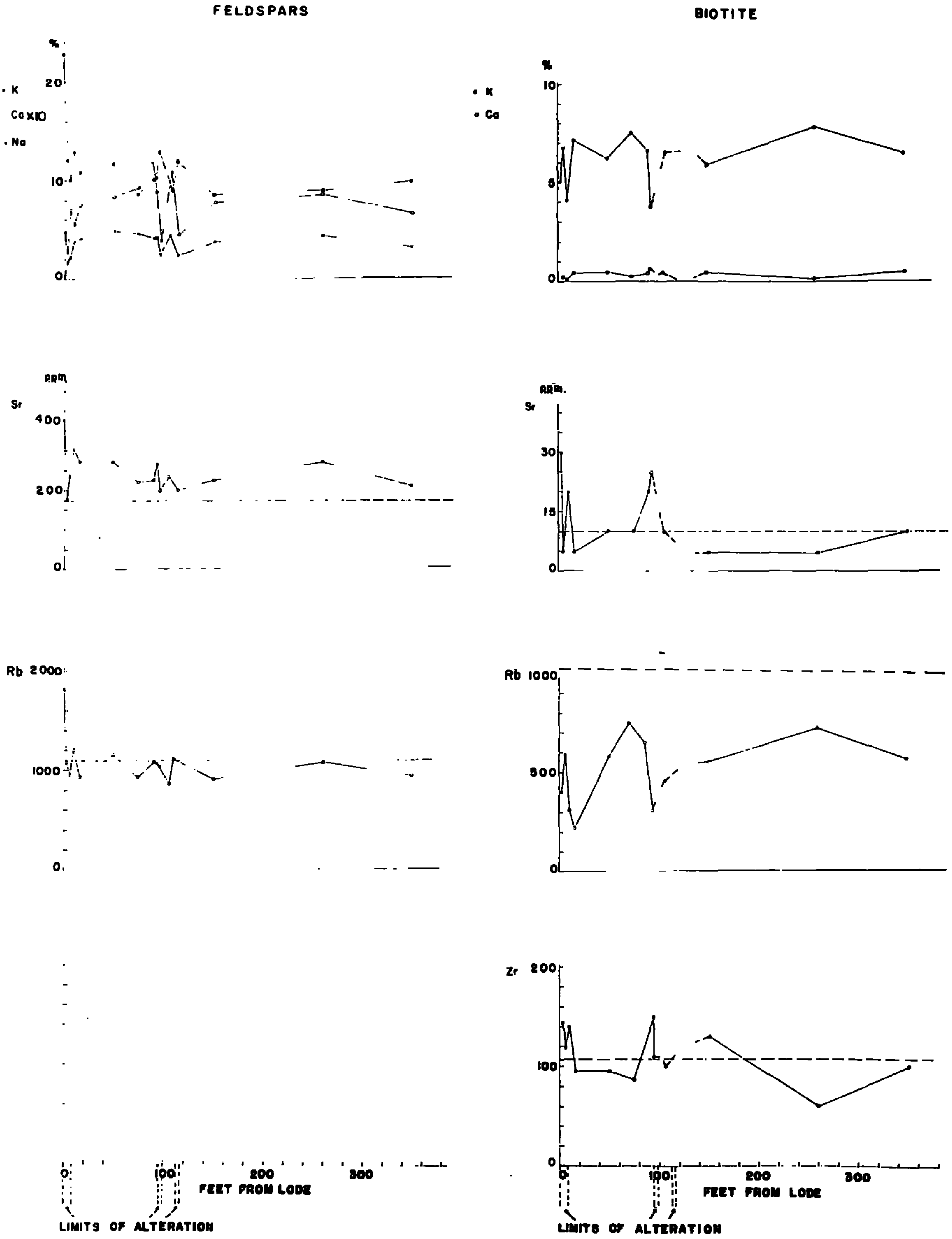

DIAGRAM 29 WALL ROCK ALTERATION, GEEVOR MINE

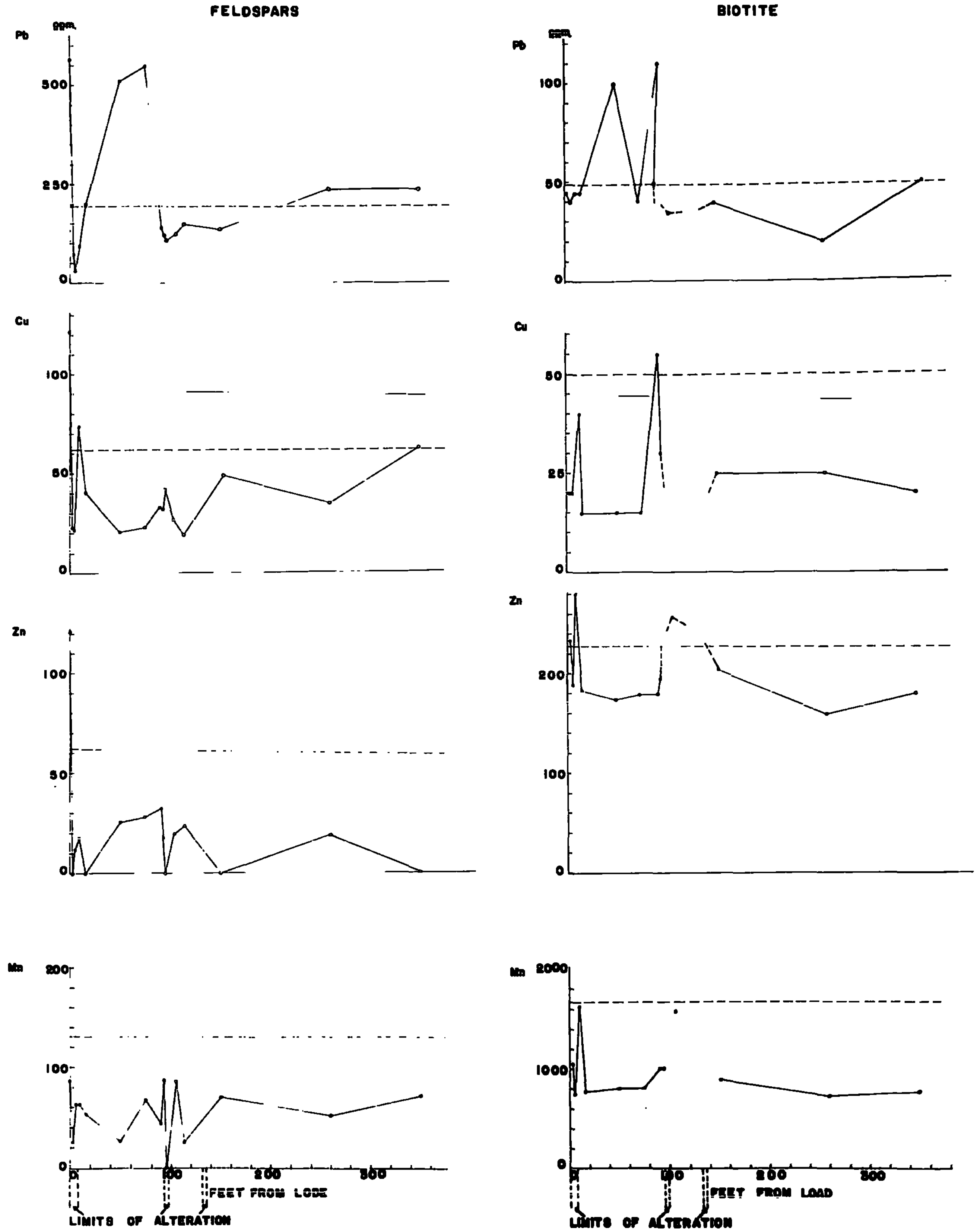

DIAGRAM 29 (CONTINUED)

low to allow separation and analysis. As for the feldspars, outside the alteration zone the potassium and calcium analyses remain practically constant.

Strontium

The strontium concentration follows the calcium results but with one exception, which is the feldspar sample adjacent to the mineral lode where strontium shows a large enrichment instead of the depletion shown by calcium. The strontium results agree closely with those given by Rao for total rock, including showing an enrichment in strontium on the edge of the unaltered granite just before the depletion in the alteration zone and following enrichment again near the vein, otherwise the strontium results are more or less uniform about the average for the Lands End granite.

Rubidium

The rubidium concentration in the feldspars follows the potassium concentration almost exactly showing a small enrichment in the two narrow alteration zones and a large enrichment next to the mineral vein. This is what might be expected after the agreement already shown between potassium and rubidium in feldspar. The rubidium concentration in the biotite also follows the potassium concentration very closely, the only anomaly being that rubidium in biotite is considerably below the average concentration for Lands End. Both feldspar and biotite show the same enrichment at the edge of the unaltered granite as strontium followed by a depletion in the alteration zone and a sharp increase adjacent to the mineral vein itself. Rao reports practically uniform rubidium values for both the feldspar and biotite fraction.

Zirconium

Zirconium was only above the detectability limit in the biotite samples where it shows little deviation from the average for the Lands End granite except directly adjacent to the alteration zone. It does appear however, that zirconium is on the upward trend as the mineral vein is approached.

Lead

Lead shows a high concentration on the edge of the mineral lode itself, and for both biotite and feldspar shows a low in the alteration zone followed by a high in the fresh granite. Other than this, lead is more or less uniform throughout the traverse. Particularly for the feldspar fraction Rao reports the same trend as established here.

Copper

As might be expected from the lack of agreement between the mineralisation and copper concentration for all the granites studied, the copper content of both the feldspar and biotite fraction near the mineral vein is equal or below the average for the Lands End granite. Particularly for the feldspar analyses the results show quite a random scatter.

Zinc

Like lead, zinc shows a high for the feldspar sample from the mineral vein but otherwise is low, with values below the average for the Lands End granite. The biotite samples show much the same distribution as many of the elements already discussed in showing a high value in the fresh granite directly adjacent to the alteration zone and low in the alteration zone itself, otherwise its values fluctuate about the average for the Lands End granite.

Manganese

Manganese follows zinc very closely for both biotite and feldspar and shows the same high at the mineral vein, low in the alteration zone and high in the adjacent unaltered granite, while beyond this manganese is below the average value for the Lands End granite.

A trend common to practically all the trace elements studied zinc in feldspar and manganese excluded, is the high concentrations directly adjacent to the mineral vein and in the unaltered granite about 7 feet away with low values in between. One possible explanation for this recurring pattern is that, following the emplacement of the ore material the distribution of most trace elements (i.e those elements present in the ore forming material) was of Reitan's type a. It is possible that associated with the ore forming stage and continuing for some time after wards was a period of hydrothermal alteration and continued movement of hydrothermal "fluids", which after the deposition of the ore material were capable of dissolving and carrying a limited amount of material; e.g. these fluids which had deposited their material at greater depth would be moving upwards relatively low in dissolved elements, although the "fluid" may have lost a great deal of its "carrying" power due to a drop in temperature and/or related factors, it was probably capable of removing loosely bonded elements from the alteration zone leaving the presently observed pattern. But, whatever the cause of the low trace element content in the alteration zone there can be little doubt that the distribution pattern was of the type shown by Reitan in his diagram a.

Another observation possible from the results of this present study is that, because of the very small effect that the ore forming activities had on the trace element content of the surrounding granite, (the aureoles established being so narrow), that primary cycle geochemical prospecting will be of little use in locating exactly new ore deposits.

Chapter 4

Conclusions

The findings of this study can be divided roughly into three groups, 1. those of direct use for geochemical prospecting in the areas studied (e.g. the high trace lead anomalies etc.); 2. those which can be used as general principles of primary dispersion geochemical prospecting and applied to most similar areas (e.g. the number of samples required to analyse a stock adequately etc.); and 3. those of only INdirect application ~~to geochemical~~ exploration; e.g. some indication of the degree of fractionation of a granite stock etc. The pertinent points of each group are summarised in turn.

The presence of syngenetic lead and zinc deposits of Cornwall were found to give significant primary dispersion geochemical anomalies indicating their presence, but the syngenetic copper deposits did not give similar anomalies and the trace nickel content likewise was average for the Cornwall area. The analyses also showed that the tested Caledonian granites are barren of concentrations of these metals. Because the British granites have been well explored in the past it can be seen that this survey was successful in detecting syngenetic lead and zinc mineralisation associated with the Cornish granite and likewise showed no syngenetic lead, zinc, copper or nickel mineralisation associated with the Caledonian granites. In all the survey only failed to detect the presence of copper in the Cornwall area giving an accurate prediction seven times out of eight. It must be emphasised however, that the actual concentrations of lead, zinc, copper etc. established here, while giving some indication of the concentration levels which can be expected in other similar areas can not be applied universally, and an "orientation survey" as already described must be carried out first in each new area to establish the relative levels of trace element concentration. The present analyses do indicate however, that either the feldspar or biotite or muscovite fractions may be used, generally with about equal accuracy, and normally a difference of about 100% exists between the trace element population in mineralised and non-mineralised granites. In addition to comparing mineralised and non-mineralised granites the present study has shown itself capable of detecting an aureole of high trace heavy metals away from the mineral vein. The aureole however, is very little wider than the easily observed alteration zone of the granite and therefore is of no real practical use.

Several details which can be applied more or less universally to primary dispersion geochemical prospecting in granites have been established, namely the number of samples required to get an adequate representation of a stock, the variation of trace elements within a given granite stock, and the difference which can be observed as significant between two means. All these questions are, of course, interlinked. While several granites (notably the Carnmenellis and Aberdeen) show a strong trace element uniformity throughout, others (e.g. Shap) are far more variable. There does not appear to be any relationship between trace element variability and size of the stock, grain size of the granite etc. and even petrographic variations of the rock type observed in hand specimen sometimes appear to have little or no effect on the variation of the trace element content. Furthermore this variability seems to have only a slight effect on the number of samples required to detect a given difference between means as significant. Using the Wilcoxon two sample test for the unpaired case it was found that about 10 samples were required to detect a difference (at the 95% probability level) in means of 50% for any trace element and 10% for major elements. As differences of about 100% are generally required in trace element means before a value is considered anomalous and probably representing proximity to mineralisation a sample density which will detect 50% difference is quite adequate. It is even possible that for a purely reconnaisance survey 5 samples would be sufficient to indicate whether or not a follow-up survey was required. It also appears from the present work that the variation in a small part of one stock or phase (i.e. about 20% of the surface area) is likely to be as great as the variation over the whole stock or phase. It may be concluded from this, that for a preliminary geochemical survey about 10 samples, no matter what the variability within the stock, even if all the samples come from a small part of the intrusion or phase, will prove adequate to represent the whole intrusion or phase.

During the course of the present investigation data was also collected to allow an estimate, at least by comparison, of the degree of fractionation, of the different granites. While no particularly new or different method for determining the degree of fractionation was found the K/Rb and Ca/Sr ratios in particular proved the most useful. Although a slightly different pattern was established for the K/Rb ratio than that given by Heier and Adams (1964), the basic interpretation remains the same. Another point of interest is the established movement of the ore "fluid" from the vein into the wall rock after allowing for the added complication of leaching in the mineral vein, this is in agreement with similar observations made by Rao (1952) and other workers, and demonstrates the practicability of establishing this point by applied geochemistry.

On the local scale the present survey has confirmed the order of intrusion of the different phases of the St. Austell granite as established by Exely (1958) and the fractionation trend from the margin to the centre of the Criffell-Dalbeattie granodiorite as established by Phillips (1956). On the other hand the divisions established by Gosh (1934) for zones 1 and 2 of the Carnmenellis granite were not confirmed by the present survey, both zones showing an equal distribution of trace and major elements; this being in agreement with modal analyses carried out by Chayes (1955). Similarly, the petrological and structural similarities that led Kennedy (1946) to conclude that the Foyers and Strontian granites had originally been one could not be detected in either the trace or major element analyses of the two granites, and on this basis, from the present information it must be concluded that the Foyers and Strontian granites were not joined at any time.

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Appendix I

Some trace and major element analyses of the feldspars, biotites and muscovites of certain British granites

The first part of this appendix lists the location of each sample with a short description of the rock type, including any visible effects due to weathering, presence of ore minerals etc. Reference is made to any identification by other authors where this is referred to in the body of the text. Following this the trace element analyses are given, first the feldspars, then the biotites and the muscovites. The last set of data gives the modal analyses of the feldspar, plus quartz powders. The sample numbers are always given in the same order, which grouping was originally devised to keep samples from the same stock, and further from the same phase of the same stock together. Certain sample numbers are missing, these gaps represent samples collected in the field but not analysed, generally because they were judged to be too weathered to be included in the present study.

Where quarries are referred to they are presently in use unless otherwise indicated.

The abbreviations used include:-

f.g.	fine grained
m.g.	medium grained
c.g.	coarse grained
n.d.	not detected, i.e. less than half the detectability limit
Tr	trace, i.e. between the detectability limit and half the detectability limit.
ud	undetermined, this usually refers to the An composition and percent microcline where the peaks were too small to estimate these values.
-	this value not recorded.

Appendix I

Dartmoor Granite

C-3	(SX 760765)	Quarry near Haytor Vale, m.g. gray granite.
C-5	(SX 345752)	Merrivale quarry, m.g. to c.g. light gray granite.
C-60	(SX 582745)	Princeton Jail Quarry, gray porphyritic granite.
C-61	(SX 564746)	Abandoned quarry near Merrivale, c.g. gray granite.
C-62	(SX 558733)	Burrator quarry, c.g. gray porphyritic granite.
C-65	(SX 745861)	Blackingstone quarry, m.g. gray porphyritic granite.
C-59	(SX 431713)	Small stock 1 mi. W. of Dartmoor granite. Road cut on A390 near Gunnislake, m.g. gray granite.

Bodmin Moor Granite

C-11	(SX 231704)	Drill core (from 44'), slight weathering of feldspars to light pink, gray porphyritic granite.
C-12	(SX 254713)	Abandoned quarry near S. Phoenax, c.g. gray granite.
C-13	(SX 260743)	Quarry near Henwood, c.g. gray granite.

St. Austell Granite

C-16	(SX 051590)	Luxulian quarry, m.g. gray porphyritic. (Biotite muscovite granite, Exely 1958).
C-18	(SX 068578)	Abandoned quarry near Luxulian, c.g. gray porphyritic (Biotite muscovite granite, Exely 1958).
C-52	(SW 917564)	Meledor china clay pit, feldspars slightly altered, m.g. gray. (Early lithionite granite, Exely 1958).
C-53	(SX 057603)	Quarry N. of Luxulian, c.g. gray porphyritic (Biotite muscovite granite, Exely 1958).
C-54	(SX 035557)	Quarry near Trethury, c.g. gray porphyritic. (Late lithionite granite, Exely 1958).
C-55	(SW 944555)	Thethosa china clay quarry, feldspar slightly altered. (Late lithionite granite, Exely 1958).

Carnmenellis Granite

C-20 (SW 741347)	Quarry near Long Downs, m.g. to c.g porphyritic (Zone 1, Gosh 1934).
C-21 (SW 726314)	Abandoned quarry near Rutteress Downs, m.g. to c.g. light gray. (Zone 1, Gosh 1934).
C-22 (SW 719314)	Quarry near Rutteress Downs, m.g. to c.g. light gray. (Zone 1, Gosh 1934).
C-23 (SW 723319)	Abandoned quarry near Rutteress Downs, m.g. to c.g. light gray. (Boarder of Zones 1 and 2, Gosh 1934)
C-24 (SW 722294)	Quarry near Brill, m.g. to c.g. light gray. (Border of Zones 1 and 2, Gosh 1934).
C-25 (SW 737307)	Quarry near Brill, m.g. to c.g. light gray. (Border of Zones 1 and 2, Gosh 1934).
C-26 (SW 742312)	Abandoned quarry near Jobs Water, m.g. to c.g. light gray. (Zone 1, Gosh 1934).
C-27 (SW 760337)	Quarry near Burnthouse, m.g. to c.g. light gray. (Zone 2, Gosh 1934).
C-28 (SW 743322)	Quarry near Long Downs, m.g. light gray. (Zone 1, Gosh 1934).
C-30 (SW 666301)	Quarry near Long Stone, m.g. to c.g. light gray. (Zone 1, Gosh 1934).
C-32 (SW 721362)	Construction site near Trembroath, f.g. to m.g. light gray porphyritic (Zone 3, Gosh 1934).
C-34 (SW 689409)	Abandoned quarry near Carnbrea Castle, Carnbrea stock ½ mi. N.W. of St. Austell stock, m.g. gray.
C-36 (SW 721412)	Carn Marth quarry, Carn Marth stock ¾ mi. N. of St. Austell stock, m.g. light gray porphyritic.
C-37 (SW 657372)	Holeman experimental mine, c.g. light gray. (Zone 1, Gosh 1934).
C-50 (SW 715290)	Abandoned quarry near Brill, m.g. to c.g. light gray (Zone 2, Gosh 1934).
C-51 (SW 749298)	Abandoned quarry near Brill, m.g. to c.g. light gray. (Zone 2, Gosh 1934).

C-56 (SW 735343)	In Long Downs abandoned quarry, m.g. to c.g. light gray porphyritic. (Zone 1, Gosh
C-57 (SW 746348)	Quarry near Long Downs, m.g. to c.g. light gray porphyritic. (Zone, 1 Gosh 1934).

Lands End Granite

C-43 (SW 449238)	Abandoned quarry at Lamorna Cove, m.g. dark gray porphyritic.
C-44 (SW 382275)	Abandoned quarry near Treave, m.g. light gray.
C-46A(SW 377347)	Geevor Mine, 3' from N. Peak lode, feldspar slightly altered to reddish pink, m.g. to c.g. porphyritic.
C-46B(" ")	Geevor Mine, 6' from N. Peak lode, m.g. to c.g. porphyritic.
C-46C(" ")	Geevor Mine, 40' from Grenville lode, m.g. to c.g. porphyritic.
C-48A(SW 489345)	Castle an Dinas quarry, f.g. tourmaline biotite granite, feldspar slightly altered.
C-48B(" ")	Castle an Dinas quarry, f.g. tourmaline biotite granite, feldspar stained a deep red.
C-48C(" ")	Castle an Dinas quarry, f.g. biotite tourmaline porphyry, slight alteration of feldspars.
C-49 (SW 377347)	The following samples C-49A to O are all taken from the cross-cut E. of lode Pb4 Geevor Mine. Distances were measured from the edge of the mineralised area.
A	0', feldspars very altered to a deep red, all biotite removed but much chlorite present, may contain some desseminated cassiterite, c.g. porphyritic.
B	2½', feldspars altered to a deep red, minor biotite and some chlorite, c.g. porphyritic.
C	4½', feldspars altered to a deep red, biotite with minor chlorite, c.g. porphyritic.

D	8½', unaltered c.g. gray biotite porphyry with minor chlorite. The transition from altered red granite to unaltered gray is very sharp and occurs at about 6' from the mineral vein edge.
E	15½', unaltered c.g. gray biotite porphyry with minor chlorite.
F	50', unaltered c.g. gray biotite porphyry with minor chlorite.
G	75', unaltered c.g. gray biotite porphyry with minor chlorite.
H	91½' (3½' from the centre of the "95'" lode), unaltered c.g. gray biotite porphyry with minor chlorite.
I	93' (22" from the centre of the "95'" lode), unaltered c.g. gray biotite porphyry with minor chlorite.
J	93½' (18" from the centre of the "95'" lode), feldspars altered to a deep red and almost all biotite removed but some chlorite present, c.g. porphyritic. The "95'" lode is approx. 6" wide consisting of quartz with associated disseminated cassiterite and is uneconomic, from the strike it probably joins lode Pb4 95' S. of the cross-cut lode junction. Alteration of the feldspars spreads to about 1½' either side of the vein.
K	105', unaltered c.g. gray biotite porphyry with associated chlorite.
L	115', feldspars altered to a deep red and almost all biotite removed but minor chlorite present, may contain minor cassiterite. This vein is a total of about 2" wide and may contain minor disseminated cassiterite. It probably joins the "95'" lode.
M	150', unaltered c.g. gray biotite porphry with associated chlorite.
N	260', slight pink alteration of the feldspars, c.g. biotite porphyry with associated chlorite.

After the "95'" lode there are no more veins

	bearing cassiterite although there are several small veins (about 1' wide) with the feldspars altered red.
O	350', unaltered c.g. gray biotite porphyry with associated chlorite.

Cligga Head Granite

C-58 (SW 737537)	From dump of exploration shaft sunk in 1960. f.g. to m.g. biotite porphyry showing slight alteration of feldspars, chalcopyrite associated.

Weardale Granite

W-1 (NY 937427)	Rookhope borehole, 1374', m.g. muscovite granite showing foliation and slight green alteration of the feldspars. Sample 2" from a ½" fluorite plus hematite vein.
W-2 "	Rookhope borehole, 1376½', m.g. muscovite granite showing foliation and slight green alteration of the feldspars.
W-3 "	1379½', Rookhope borehole, m.g. muscovite granite showing foliation and slight green alteration of the feldspars. Sample 2" from a ¼" fluorite (and hematite) vein.
W-4 "	1386½', Rookhope borehole, m.g. muscovite biotite granite showing foliation.
W-5 "	Rookhope borehole, 1395', m.g. muscovite biotite granite showing foliation.
W-6 "	Rookhope borehole, 1451', m.g. muscovite granite showing foliation. Sample 3" from a joint face showing galena.
W-7 "	Rookhope borehole, 2259', m.g. muscovite biotite granite.
W-8 (NY 937427)	Rookhope borehole, 2849', m.g. muscovite biotite granite.

Shap Granite

Shap 1 (NY 557084)	Shap quarry, m.g. porphyritic adamellite.

Shap 2	(NY 557084)	Shap quarry, m.g. porphyritic adamellite.
Shap 3	"	Shap quarry, m.g. porphyritic adamellite.
Shap 4	"	Shap quarry, m.g. porphyritic adamellite.

Criffell-Dalbeattie Granodiorite

D-1	(NX 964692)	Abandoned quarry near New Abby, m.g. pink granite, feldspars showing red alteration. (Main granodiorite, Phillips 1956).
D-2	(NX 959647)	Abandoned quarry in New Abby, m.g. gray. Main granodiorite, Phillips 1956).
D-4	(NX 885558)	Abandoned quarry near Sandyhill, m.g. gray. (Main granodiorite, Phillips 1956).
D-5	(NX 842553)	Abandoned quarry near Kippford, m.g. gray. (Main granodiorite, Phillips 1956).
D-11	(NX 803535)	Road under construction, f.g. dark. (Main granodiorite, Phillips 1956).
D-14	(NX 897685)	Abandoned quarry near Beeswing, m.g. gray. (Main granodiorite, Phillips 1956).
D-15	(NX 954656)	Excavation under construction, m.g. gray. (Main granodiorite, Phillips 1956).
D-12	(NX 802532)	Road under construction, m.g. light gray. (Contact of main and intermediate granodiorite, Phillips 1956).
D-6	(NX 835592)	Road cut near Dalbeattie, c.g. gray porphyry, some red alteration to the feldspars. (Porphyritic granodiorite, Phillips 1956).
D-8	(NX 851593)	Quarry in Dalbeattie Forest, c.g. gray porphyry, some red alteration to the feldspars. (Porphyritic granodiorite, Phillips 1956).
D-9	(NX 827617)	Quarry near Dalbeattie, c.g. gray porphyry, very slight alteration of feldspars to pink. (Porphyritic granodiorite, Phillips 1956).
D-10	(NX 819609)	Quarry near Dalbeattie, c.g. gray porphyry. (Porphyritic granodiorite, Phillips 1956).

D-13	(NX 853638)	Abandoned quarry near Southwick, c.g. gray porphyry. (Porphyritic granodiorite, Phillips).
D-3	(NX 922567)	Quarry near Chalkbush, f.g. pink aplite dyke.

Etive Complex

Allt na Lairige Granite

E-1	(NN 255173)	Quarry at Allt na Lairige dam, m.g. gray porphyritic granite.
E-2	(NN 237169)	Road cut, m.g. gray porphyritic granite.
E-3	(NN 234165)	Road cut, m.g. gray porphyritic granite, slight pink alteration to feldspars.

Ballachulish Granite

E-19	(NN 014584)	Road cut near Kentallen, m.g. gray biotite granite.
E-20	(NN 032595)	Road cut near Ballachulish, m.g. gray biotite granite.
E-22	(NN 032590)	New road in Ballachulish Forest, m.g. gray biotite granite.
E-21	(NN 041572)	New road in Ballachulish Forest, m.g. gray biotite granite.

Cruachan Granite

According to the map given by Anderson (1937) all the following samples fall in the Cruachan granite of the Etive Complex.

E-7	(NN 081318)	Noe W. tunnel, 1715' from junction with E. tunnel, m.g. gray biotite granite.
E-8	(NN 092317)	Noe E. tunnel, 2218' from junction, m.g. gray granite.
E-12	(NN 112319)	Entrance of Mhoille intake tunnel, m.g. gray biotite granite.
E-13	(NN 121315)	Cut in access road to Mhoille intake tunnel, m.g. gray biotite granite.

E-14 (NN 039308)	Inverawe tunnel scheme drill core, m.g. gray biotite granite, chalcopyrite on joint face.
E-15 (NN 026318)	Bore hole near Inverawe house, m.g. gray biotite granite, slight pink alteration to feldspars, 30' from phyllite contact.
E-9 (NN 085316)	Junction of Noe E. and W. tunnels, m.g. light pink biotite granite.
E-10 (NN 085305)	3260' from entrance of Noe tunnel, m.g. light pink biotite granite.
E-11 (NN 083295)	50' from entrance of Noe tunnel, m.g. pink biotite granite, feldspar quite altered. Sample from edge of Anderson's Zone of Complication.
E-16 (NN 045367)	Road cut on N. side of Loch Etive, c.g. light pink biotite granite.
E-23A(NN 208514)	Road cut, Glen Etive, m.g. light pink biotite granite, feldspars quite altered.
E-24 (NN 245546)	Road cut, Glen Etive, f.g. gray granite, feldspars quite altered.
E-23B(NN 208514)	Same location as E-23A, small aplite dyke.

Strontián Granite Complex

S-16 (NM 851527)	Kingarloch pier quarry, m.g. pink, feldspars show considerable alteration. (Biotite granite, Sabine 1963).
S-2 (NM 863530)	Road cut near Glengalmadale, m.g. pink foliated porphyry. (Biotite granite, Sabine 1963).
S-13 (NM 822619)	Road cut near Strontián, c.g. gray porphyry. (Porphyritic granodiorite, Sabine 1963).
S-15 (NM 759538)	Fresh road cut near Beach farm, c.g. gray porphyry. (Porphyritic granodiorite, Sabine).
S-31 (NM 826544)	Road cut near Loch Uisage, c.g. gray porphyry. (Porphyritic granodiorite, Sabine 1963).
S-4 (NM 782557)	Road cut at junction of B8043 and A884, c.g. gray porphyry. (Porphyritic granodiorite, Sabine 1963).

S-5	(NM 782595)	Road cut near Liddesdale, c.g. gray porphyry. (Porphyritic granodiorite, Sabine 1963).
S-6	(NM 808602)	Road cut on S. side of Loch Sunart, c.g. gray porphyry. (Porphyritic granodiorite, Sabine).
S-7	(NM 796613)	Road cut on N. Side of Loch Sunart, c.g. gray porphyry. (Porphyritic granodiorite, Sabine).
S-8	(NM 863604)	Exposure in Carnoch R, m.g. gray.(Tonalite, Sabine 1963).
S-10	(NM 825658)	Drill core near old Pb mines, samples about 100' from vein, m.g. gray foliated. (Tonalite, Sabine 1963).
S-11	(NM 833658)	Drill core near old Pb mine, sample about 100' from vein, m.g. gray foliated. (Tonalite, Sabine, 1963).
S-12	(NM 838657)	Drill core near old Pb mines, samples about 100' from vein, m.g. gray foliated. (Tonalite, Sabine 1963).
S-14	(NM 742504)	Exposure in Amhainn a'Ghlinne Ghil, recently blasted, m.g. gray foliated. (Tonalite, Sabine 1963).

Foyers Granite Complex

F-1	(NH 523157)	Drill core near River,E, 453', m.g. gray foliated minor red alteration of feldspars. (Tonalite, Pochin Mould, 1948).
F-4A	(NH 572239)	Drill core, 40', m.g. gray. (Tonalite, Pochin Mould 1948).
F-4B	(NH 572239)	As F-4A, 70', m.g. gray, feldspars show some pink alteration. (Tonalite, Pochin Mould, 1948).
F-5	(NH 571232)	Drill core, m.g. gray, feldspars show some pink alteration. (Tonalite, Pochin Mould, 1948).
F-6	(NH 570233)	Drill core, m.g. light pink, feldspars show some alteration. (Tonalite, Pochin Mould, 1948).
F-8	(NH 548205)	Abandoned quarry near Loch Mhor, m.g. gray, slight alteration. (Tonalite, Pochin Mould).

F-9	(NH 548227)	Road cut, m.g. gray foliated, slight alteration. (Tonalite, Pochin Mould 1948).
F-2	(NH 512183)	Drill core, 590', c.g. gray porphyritic. (Porphyritic granodiorite, Pochin Mould 1948).
F-3	(NH 522175)	Drill core, 19', c.g. gray porphyritic. (Porphyritic granodiorite, Pochin Mould 1948).
F-7	(NH 510190)	Drill core, 56', c.g. gray porphyritic. (Porphyritic granodiorite, Pochin Mould 1948).
F-10	(NH 523225)	Road cut in Farigaig forest, c.g. gray porphyritic. (Porphyritic granodiorite, Pochin Mould 1948).

Cluanie Granodiorite

All samples are from fresh exposures made by the construction of a new dam site and road in 1961.

Cl-1	(NH 143100)	Road cut, specimen about 100' from contact, m.g. white hornblende granodiorite (Leedal 1952).
Cl-2	(NH 151104)	Road cut, pink m.g. hornblende granodiorite (Leedal 1952).
Cl-3	(NH 163106)	Road cut, m.g. pink hornblende biotite granodiorite (Leedal 1952).
Cl-4	(NH 173105)	Road cut, m.g. pink hornblende biotite granodiorite (Leedal 1952).
Cl-5	(NH 182106)	Quarry, m.g. pink hornblende biotite granodiorite (Leedal 1952).
Cl-6	(NH 185095)	Dam site, m.g. pink hornblende granodiorite (Leedal 1952).
Cl-7	(NH 189012)	Road cut, specimen about 110' from contact, m.g. white hornblende granodiorite (Leedal 1952).

Aberdeen Area

Granton Granite

A-1	(NJ 024323)	Road cut near Huntly Cave, f.g. light gray biotite muscovite granite.

Aberdeen (or Hill of Fare) Granite

A-2	(NJ 912055)	Rubislaw quarry, m.g. gray. (Gray granite, Bisset 1932).
A-3	(NJ 899093)	Bucksburn quarry, m.g. gray. (Gray granite, Bisset 1932).
A-4	(NJ 866137)	Dyce quarry (abandoned), m.g. gray. (Gray granite, Bisset 1932).
A-7	(NJ 765168)	Abandoned quarry near Kintore, m.g. gray. (Gray granite, Bisset 1932).
A-8	(NJ 738170)	Kemney quarry, ~~m.g. gray.~~ (Gray granite, Bisset 1932).
A-9A	(NJ 642118)	Corrennie quarry, m.g. gray. (Gray granite, Bisset 1932).
A-9B	(NJ 642118)	As above, c.g. red granite penetrating the gray granite, transition zone quite wide. (Bisset 1932).
A-10	(NJ 732093)	Graiginlow quarry, m.g. gray porphyry. (Porphyritic granite, Bisset 1932).
A-5	(NH 846110)	Tyrebagger quarry, m.g. pink. (Transition between gray and porphyritic granite, Bisset).
A-6	(NJ 836124)	Blackburn quarry (abandoned), m.g. pink. (Transition between gray and porphyritic granite, Bisset 1932).
A-11	(NJ 717052)	Sunhoney quarry, (abandoned), c.g. red. (Red granite, Bisset 1932).
A-12	(NJ 712003)	Abandoned quarry near Hattonburn, c.g. red. (Red granite, Bisset 1932).
A-20	(NJ 526061)	Abandoned quarry near Tarland, m.g. pink granite.
A-21	(NJ 487035)	Abandoned quarry near Tarland, m.g. gray granite.
A-19	(NJ 935025)	Quarry in small stock S. of Aberdeen, m.g. red granite.

Peterhead Granite

A-14 (NK 124410)	Stirling hill quarries (abandoned), c.g. red granite.
A-15 (NK 067506)	Abandoned quarry near Rora, c.g. gray granite.
A-16 (NJ 973478)	Abandoned quarry near Old Deer, f.g. gray granite.

Fraserburgh Granite

A-17 (NJ 897563)	New Pitsligo quarry, m.g. gray granite.
A-18 (NJ 912600)	Blackrigg quarry, m.g. gray granite.

Strathdearn (or Findhorn) Granite

A-24 (NH 748216)	Drill core near River Findhorn, m.g. gray granite.
A-25 (NH 747217)	Drill core near River Findhorn, gray porphyritic granite.

Feldspar Results

The feldspar results are given in two sections, first the quantitative results as determined by x-ray fluorescence and flame photometry, and second, the modal analyses for plagioclase, microcline, orthoclase, anorthite and quartz, measured on the x-ray diffractometer.

Feldspar, quantitative analyses

All values have been recalculated knowing the percentage of quartz in each powder (as recorded in the next section) and assuming quartz to be free from any of the elements analysed for.

Feldspar, quantitative results

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
Dartmoor											
C-3	254	715	91	61	nd	nd	250	nd	5.11	7.04	1.75
C-5	18	999	47	56	56	nd	131	nd	-	-	-
C-60	191	577	100	13	18	nd	144	64	4.60	7.55	1.67
C-61	94	938	122	43	31	nd	281	29	4.53	7.87	1.02
C-62	69	1066	93	nd	22	nd	89	49	4.93	8.39	0.84
C-63	207	967	140	37	47	nd	135	135	4.43	9.30	0.98
C-65	254	681	160	nd	34	nd	91	32	5.54	7.99	2.25
C-59	109	998	91.1	15	30	nd	150	30	5.75	6.38	.80
Bodmin											
C-11	222	890	275	44	44	nd	111	31	5.45	9.20	1.25
C-12	311	840	328	19	28	nd	111	31	6.59	7.65	1.95
C-13	280	839	238	16	58	nd	144	nd	4.94	8.69	0.77
St. Austell											
C-16	117	668	128	15	52	nd	130	nd	5.38	8.35	1.52
C-18	364	857	127	26	nd	nd	45	nd	4.09	10.69	.90
C-52	165	441	41	21	35	nd	50	71	6.70	5.82	0.94
C-53	268	838	115	18	33	nd	110	60	5.70	8.68	1.70
C-54	61	1045	170	15	39	nd	121	148	5.70	6.91	0.76
C-55	48	1690	42	14	52	nd	52	48	5.72	6.10	0.40
Carnmenellis											
C-20	265	744	159	nd	20	nd	59	nd	5.04	9.17	1.31
C-21	203	783	254	19	nd	nd	nd	nd	5.27	8.02	0.86
C-22	227	772	150	nd	25	nd	59	nd	4.78	7.68	1.08
C-23	336	1071	211	nd	47	nd	70	nd	4.96	8.80	0.23
C-24	245	835	194	38	87	nd	62	nd	4.96	8.16	1.30

Feldspars, quantitative results (continued)

Carnmenellis

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
C-25	528	809	171	24	43	nd	57	nd	5.48	6.40	2.09
C-26	491	832	173	16	nd	nd	107	nd	5.11	7.66	1.42
C-27	255	766	195	27	nd	nd	64	nd	4.75	7.88	1.24
C-28	325	753	175	nd	53	nd	93	nd	6.08	8.88	1.63
C-30	232	1156	264	27	nd	nd	189	nd	5.67	9.59	1.13
C-32	316	894	342	29	55	nd	63	29	2.97	9.42	1.16
C-34	360	962	184	32	37	Tr	92	nd	5.34	9.52	1.10
C-36	260	1058	400	63	nd	nd	114	nd	6.23	9.89	1.26
C-37	250	930	200	34	nd	nd	84	nd	4.04	9.03	0.89
C-50	274	771	134	nd	21	nd	62	51	4.45	7.31	1.24
C-51	262	666	160	nd	52	nd	37	60	4.41	6.61	1.35
C-56	143	810	51	nd	42	nd	56	40	4.51	6.61	0.78
C-57	107	839	152	nd	35	nd	26	33	4.64	7.68	1.17

Lands End

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
C-43	286	1189	323	92	nd	nd	189	nd	5.26	11.93	1.06
C-44	38	2173	58	40	25	nd	128	nd	5.65	7.00	0.45
C-46A	224	755	153	22	22	nd	74	nd	4.02	7.68	0.68
C-46B	266	991	118	31	38	nd	49	nd	2.76	10.65	0.41
C-46C	236	994	170	73	nd	nd	109	nd	4.29	9.94	1.09
C-48A	114	1044	52	45	nd	nd	102	nd	4.02	6.90	0.61
C-48B	98	1291	69	nd	48	nd	221	nd	2.10	11.91	0.43
C-48C	148	1400	636	194	30	nd	185	nd	5.24	10.06	0.86
C-49											
C-49A	378	1827	566	157	131	nd	96	87	.435	20.66	0.48
C-49B	179	1060	72	nd	23	nd	40	26	1.79	12.19	0.28
C-49C	233	955	31	13	22	nd	40	63	2.22	10.15	0.71
C-49D	305	1222	95	18	74	nd	58	63	3.84	13.04	0.58
C-49E	275	942	200	nd	41	nd	84	54	4.04	10.81	0.77
C-49F	271	1157	513	26	21	nd	68	29	4.71	11.76	0.84

Feldspar, quantitative results (continued)

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
Lands End											
C-49G	221	932	548	28	23	nd	103	68	4.36	8.71	0.93
C-49H	244	1088	140	33	33	nd	82	44	4.28	10.17	1.20
C-49I	268	1078	121	18	32	nd	105	89	4.29	10.39	0.89
C-49J	200	1043	106	nd	42	nd	47	nd	2.50	13.15	0.39
C-49K	235	866	124	20	27	nd	73	87	4.51	9.12	1.11
C-49L	200	1119	150	24	19	nd	19	26	2.48	12.02	0.45
C-49M	224	939	137	nd	49	nd	41	71	3.88	9.59	0.78
C-49N	270	1080	238	19	35	nd	59	54	4.46	11.02	0.86
C-490	208	938	238	nd	63	nd	45	73	3.18	9.90	0.65
Cligga Head											
C-58	129	1553	1035	21	29	nd	286	79	4.93	11.46	0.68
Weardale											
W-1	63	907	118	nd	63	nd	163	79	4.71	9.39	0.71
W-2	223	1088	71	nd	nd	nd	162	74	5.82	8.76	3.18
W-3	136	858	72	nd	108	nd	64	51	6.84	6.96	0.77
W-4	286	840	136	nd	nd	nd	79	25	5.33	5.74	0.50
W-5	120	1028	102	nd	18	nd	80	44	5.02	8.61	0.55
W-6	300	707	102	nd	31	nd	92	nd	4.72	6.94	0.83
W-7	233	608	123	nd	20	nd	78	39	3.33	5.78	1.10
W-8	256	727	130	nd	28	nd	48	65	3.21	7.86	0.82
Shap											
Shap 1	866	466	123	61	35	nd	65	nd	4.13	7.05	2.56
Shap 2	983	605	127	nd	38	nd	57	45	4.69	8.52	1.66
Shap 3	1032	446	154	nd	44	nd	39	53	4.81	6.97	2.17
Shap 4	922	445	73	nd	25	nd	35	40	4.72	5.99	1.72

Feldspar, quantitative results (continued)

Criffell-Dalbeattie

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
D-1	1400	194	90	14	60	nd	100	100	6.50	3.94	3.06
D-2	789	149	151	12	25	nd	30	42	5.56	4.17	3.35
D-4	2266	117	157	25	56	nd	70	31	7.67	4.39	5.45
D-5	1976	154	125	nd	46	nd	52	62	6.93	4.41	4.43
D-11	2030	37	135	nd	26	nd	30	51	8.52	2.45	4.59
D-14	2025	129	86	11	25	nd	23	17	5.31	3.22	3.25
D-15	1499	224	151	nd	53	nd	53	22	6.10	5.53	2.67
D-12	1779	158	122	nd	48	nd	48	24	6.05	5.64	3.43
D-6	926	350	106	nd	47	nd	34	21	4.91	6.88	1.81
D-8	710	394	115	13	35	nd	42	21	4.49	7.12	1.57
D-9	1271	275	152	nd	70	nd	39	25	6.06	6.06	2.86
D-10	1365	231	124	nd	62	nd	38	53	6.35	5.46	3.20
D-13	998	246	194	13	19	nd	243	38	5.43	5.51	2.82
D-3	155	343	66	9	25	nd	375	56	5.16	3.75	.28

Etive Complex

Allt na Lairige

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
E-1	3042	87	nd	nd	16	nd	27	17	6.24	2.70	2.65
E-2	3114	130	208	nd	22	nd	69	59	8.09	5.10	2.63
E-3	2056	144	40	nd	40	nd	79	35	6.58	4.31	1.42

Ballachulish

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
E-19	3885	24	130	nd	39	nd	41	nd	6.97	2.50	3.72
E-20	3660	40	176	nd	46	nd	32	30	6.90	3.36	4.48
E-22	3270	74	160	nd	36	nd	34	48	6.68	4.12	4.46
E-21	2856	163	117	12	39	nd	35	34	6.07	4.31	2.83

Cruachan

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
E-7	2611	56	92	nd	nd	nd	33	46	5.68	3.23	5.02
E-8	1892	67	89	nd	nd	nd	nd	nd	5.50	3.19	4.22

Feldspar, quantitative results (continued)

Cruachan

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
E-12	2017	37	55	20	23	nd	68	31	5.45	2.30	5.02
E-13	2160	14	90	nd	81	nd	23	30	5.28	1.85	5.20
E-14	438	180	56	30	140	nd	244	30	5.41	4.16	0.95
E-15	1760	200	131	69	128	nd	117	69	5.11	9.00	2.55
E-9	1895	46	122	nd	36	nd	24	16	5.61	4.09	2.56
E-10	1330	56	87	9	15	nd	26	30	5.75	3.33	2.96
E-11	914	102	75	7	13	nd	74	25	4.36	3.66	1.46
E-16	2361	141	100	nd	45	nd	39	45	5.04	6.13	3.75
E-23A	1223	356	64	nd	114	nd	nd	83	6.12	7.84	2.47
E-24	5070	35	110	12	30	nd	37	19	6.51	2.08	6.32
E-23B	133	422	111	nd	nd	nd	266	67	5.04	9.55	.36
Strontian											
S-16	1165	237	89	nd	nd	nd	27	20	5.39	5.02	2.09
S-2	1750	226	104	14	nd	nd	102	nd	7.40	5.50	1.96
S-13	2742	36	104	16	92	nd	25	36	5.74	3.10	2.99
S-15	2241	41	94	nd	39	nd	nd	34	5.33	3.48	2.85
S-3A	2360	44	84	31	14	nd	24	16	5.85	2.65	3.66
S-4	3388	28	140	20	72	nd	nd	nd	7.27	2.66	3.70
S-5	2906	46	115	nd	46	nd	22	43	6.68	3.19	3.11
S-6	2074	29	90	8	27	nd	nd	35	5.04	2.53	2.59
S-7	2806	32	111	nd	24	nd	27	nd	5.90	3.29	3.34
S-8	2668	50	102	17	46	nd	38	38	6.35	3.02	3.53
S-10	312	208	146	nd	116	nd	nd	81	4.12	6.06	2.14
S-11	2542	48	120	nd	59	nd	52	36	6.61	2.95	3.87
S-12	2202	68	120	21	42	nd	30	20	6.25	3.29	3.81
S-14	2786	nd	115	nd	49	nd	40	53	7.88	1.15	5.66
Foyers											
F-1	1969	71	118	nd	20	nd	37	51	5.02	4.60	3.99

Feldspar, quantitative results (continued)

Foyers

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
F-4A	2643	nd	75	9	29	nd	17	22	5.6	1.40	4.57
F-4B	2635	47	110	12	nd	nd	70	39	6.79	2.71	4.27
F-5	1257	30	53	nd	30	nd	49	21	3.14	6.33	2.04
F-6	672	175	57	11	66	nd	ud	ud	4.54	7.48	1.33
F-8	3004	nd	114	nd	nd	nd	51	13	5.51	1.52	4.61
F-9	2544	10	99	nd	38	nd	40	54	5.87	1.99	4.36
F-2	1864	56	109	nd	28	nd	23	37	5.40	4.09	3.24
F-3	2163	85	118	nd	32	nd	25	19	5.75	6.08	3.04
F-7	2166	76	122	16	47	nd	40	40	5.42	4.90	3.26
F-10	2419	16	105	9	23	nd	64	14	5.61	2.88	3.99

Cluanie

Cl-1	1888	97	98	nd	27	nd	nd	39	7.16	3.65	1.72
Cl-2	1593	106	109	10	23	nd	21	41	6.18	3.37	1.48
Cl-3	2045	99	110	nd	19	nd	24	36	6.72	3.02	1.96
Cl-4	1808	160	134	10	18	nd	21	34	8.21	5.44	1.44
Cl-5	2037	93	91	11	35	nd	26	44	6.84	2.68	2.37
Cl-6	1918	105	101	10	22	nd	41	15	6.11	3.40	1.96
Cl-7	958	177	90	nd	29	nd	21	41	4.23	3.39	2.02

Aberdeen

A-1	675	343	124	nd	54	nd	41	54	5.08	3.32	2.84
A-2	960	114	90	18	31	nd	33	49	5.59	4.63	3.63
A-3	1206	89	96	nd	31	nd	31	42	3.49	3.96	3.85
A-4	1096	128	113	15	39	nd	37	24	5.43	5.29	4.04
A-7	1112	168	118	nd	45	nd	34	45	5.58	6.49	2.77
A-8	734	194	104	nd	27	nd	nd	180	4.49	6.26	1.68
A-9A	1278	100	60	nd	21	nd	36	43	7.39	3.07	3.47
A-9B	394	190	81	15	25	nd	98	38	5.93	6.49	1.40
A-10	1418	72	106	nd	43	nd	28	45	6.35	4.01	3.10

Feldspar, quantitative results (continued)

	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Cr ppm	Na %	K %	Ca %
Aberdeen											
A-5	1037	165	98	19	23	nd	154	26	7.50	5.06	3.31
A-6	783	170	77	10	28	nd	76	41	5.44	4.64	2.49
A-11	54	473	49	12	40	nd	26	35	5.20	6.67	0.54
A-12	148	536	117	nd	29	nd	40	93	5.95	8.57	0.88
A-20	42	368	77	12	18	nd	32	53	4.99	7.32	0.70
A-21	1270	116	75	nd	43	nd	42	18	6.19	3.59	2.59
A-19	1198	128	121	nd	65	nd	42	58	6.27	4.52	4.54
Peterhead											
A-14	116	603	102	15	42	nd	46	23	5.12	9.14	0.56
A-15	1410	25	136	25	93	nd	182	86	6.75	1.25	ud
A-16	300	403	120	17	37	nd	37	73	4.83	8.20	2.10
Fraserburgh											
A-17	433	255	133	nd	41	nd	36	60	5.52	7.95	4.14
A-18	365	295	91	15	56	nd	33	43	5.14	7.92	2.93
Strathdearn											
A-24	1802	104	95	9	33	nd	135	55	5.10	4.48	3.82
A-25	1872	146	137	12	21	nd	166	62	6.51	4.87	3.64

Feldspar, Modal analyses

Dartmoor

	Orthoclase %	Microcline %	Plagioclase %	Anorthite %	Quartz %
C-3	25	nd	19	ud	56
C-5	-	-	-	-	55
C-60	13	12	20	30	55
C-61	30	nd	19	18	51
C-62	25	ud	20	10	55
C-63	26	ud	17	15	57
C-65	24	nd	20	23	56
C-59	26	nd	21	30	54

Bodmin

C-11	20	nd	16	15	64
C-12	nd	17	19	10	64
C-13	23	nd	20	10	57

St. Austell

C-16	23	nd	20	23	54
C-18	27	-	15	17	58
C-52	nd	17	17	1or2	66
C-53	23	nd	17	19	60
C-54	19	ud	14	2	67
C-55	27	nd	23	8	50

Carnmenellis

C-20	25	ud	24	20	51
C-21	13	8	16	20	63
C-22	30	nd	22	15	49
C-23	29	ud	12	15	53
C-24	26	ud	21	20	53
C-25	25	ud	17	15	58
C-26	25	nd	20	18	55
C-27	26	nd	19	15	55

Feldspar, Modal analyses (continued)

Carnmenellis

	Orthoclase %	Microcline %	Plagioclase %	Anorthite %	Quartz %
C-28	22	1	18	20	60
C-30	20	2	15	10	63
C-32	8	12	18	8	62
C-34	2	20	16	ud	62
C-36	12	6	17	15	65
C-37	24	3	17	15	56
C-50	23	ud	22	15	53
C-51	28	ud	20	18	52
C-56	3	30	22	ud	45
C-57	24	ud	19	20	54
Lands End					
C-43	21	ud	14	ud	65
C-44	17	4	19	ud	60
C-46A	20	2	32	15	46
C-46B	nd	28	11	ud	61
C-46C	26	nd	18	15	56
C-48A	26	nd	18	ud	56
C-48B	34	nd	12	ud	54
C-48C	9	9	15	ud	67
C-49A	23	nd	ud	nd	77
C-49B	34	ud	5	ud	57
C-49C	29	nd	13	ud	55
C-49D	22	6	10	ud	62
C-49E	32	ud	12	ud	56
C-49F	28	ud	10	ud	62
C-49G	23	3	13	ud	57
C-49H	30	nd	15	ud	55
C-49I	25	ud	13	ud	62
C-49J	26	3	7	ud	64

Feldspar, Modal analyses (continued)

	Orthoclase %	Microcline %	Plagioclase %	Anorthite %	Quartz %
Lands End					
C-49K	22	6	17	ud	55
C-49L	29	3	11	ud	58
C-49M	22	6	13	nd	59
C-49N	13	12	12	ud	63
C-49O	26	2	10	ud	60
Cligga Head					
C-58	10	10	8	ud	72
Weardale					
W-1	nd	20	18	30	62
W-2	19	ud	15	30	66
W-3	17	ud	22	30	61
W-4	2	20	22	30	56
W-5	ud	25	22	30	45
W-6	nd	20	23	35	52
W-7	ud	22	32	ud	49
W-8	ud	24	22	ud	54
Shap					
Shap 1	35	nd	22	20	43
Shap 2	28	nd	20	20	47
Shap 3	34	nd	27	20	43
Shap 4	36	nd	24	20	37
Criffell-Dalbeattie					
D-1	13	ud	35	26	50
D-2	15	3	41	25	40
D-4	ud	nd	36	28	64
D-5	12	3	35	21	52
D-11	14	nd	45	28	43
D-14	ud	18	47	ud	35

Feldspar, Modal analyses (continued)

Criffell-Dalbeattie

	Orthoclase %	Microcline %	Plagioclase %	Anorthite %	Quartz %
D-15	nd	15	32	18	51
D-12	19	ud	27	18	54
D-6	26	nd	22	26	47
D-8	nd	24	25	26	48
D-9	18	nd	25	21	56
D-10	20	nd	23	26	55
D-13	11	11	28	21	48
D-3	nd	39	42	nd	21

Etive Complex

Allt na Lairige

E-1	16	nd	50	20	36
E-2	14	nd	32	16	54
E-3	21	nd	35	20	43

Ballachulish

E-19	14	nd	40	25	50
E-20	15	nd	35	25	50
E-22	16	nd	34	25	50
E-21	18	4	41	17	38

Cruachan

E-7	17	nd	48	25	37
E-8	25	ud	44	27	33
E-12	19	nd	47	30	35
E-13	15	nd	59	30	26
E-14	13	12	50	20	28
E-15	16	nd	13	20	71
E-9	26	nd	42	-	30
E-10	23	ud	43	20	34
E-11	28	nd	9	18	21
E-16	9	10	25	25	56

Feldspar, Modal analyses (continued)

	Orthoclase %	Microcline %	Plagioclase %	Anorthite %	Quartz %
Cruachan					
E-23A	16	nd	20	20	64
E-24	12	nd	53	30	41
E-23B	23	nd	22	20	55
Strontian					
S-16	ud	21	32	13	45
S-2	16	nd	34	13	50
S-13	16	nd	56	20	33
S-15	24	nd	43	20	29
S-3A	19	nd	52	23	30
S-4	17	nd	48	20	35
S-5	23	nd	42	-	33
S-6	12	nd	70	-	18
S-7	18	nd	43	20	37
S-8	15	ud	48	25	34
S-10	23	nd	20	20	52
S-11	10	4	40	20	44
S-12	17	nd	34	18	44
S-14	ud	ud	45	25	55
Foyers					
F-1	20	nd	38	23	41
F-4A	13	nd	76	25	11
F-4B	11	nd	44	28	43
F-5	24	nd	27	23	47
F-6	33	nd	26	15	39
F-8	6	5	75	30	14
F-9	16	nd	68	25	18
F-2	24	nd	40	23	36
F-3	26	nd	30	23	41
F-7	22	nd	28	25	45
F-10	20	nd	63	28	20

Feldspar, Modal analyses (continued)

Cluanie	Orthoclase %	Microcline %	Plagioclase %	Anorthite %	Quartz %
Cl-1	24	nd	40	10	36
Cl-2	16	nd	55	10	29
Cl-3	17	2	51	13	30
Cl-4	31	nd	40	18	27
Cl-5	16	ud	50	13	34
Cl-6	20	ud	52	13	27
Cl-7	17	ud	54	20	30
Aberdeen					
A-1	nd	18	19	18	63
A-2	8	9	30	25	49
A-3	nd	14	33	25	52
A-4	20	ud	26	25	54
A-7	9	10	25	20	56
A-8	nd	23	22	18	51
A-9A	15	2	35	18	53
A-9B	nd	21	30	8	48
A-10	9	8	33	18	47
A-5	14	nd	28	15	57
A-6	21	nd	35	15	42
A-11	6	23	24	5	43
A-12	23	nd	19	ud	58
A-20	nd	30	25	25	43
A-21	nd	29	27	28	40
A-19	16	nd	27	28	57
Peterhead					
A-14	19	19	17	5	52
A-15	nd	nd	28	35	72
A-16	26	nd	15	25	59
Fraserburgh					
A-17	9	10	23	28	58

Feldspar, Modal analyses (continued)

Fraserburgh

	Orthoclase %	Microcline %	Plagioclase %	Anorthite %	Quartz %
A-18	4	18	24	25	54
Strathdearn					
A-24	21	nd	31	28	45
A-25	15	nd	33	25	52

Appendix I (continued)

Biotite Results

All samples are at least 98% pure, the remaining 2% being largely feldspar with minor muscovite.

	Zr ppm	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Na %	K %	Ca %
Dartmoor											
C-3	100	Tr	870	20	398	34	34	3420	-	-	-
C-60	40	5	1180	20	280	20	40	3500	-	9.3	0.11
C-61	nd	nd	1430	35	360	25	40	5200	-	9.5	0.12
C-62	Tr	nd	2310	30	340	35	50	4800	-	10.0	0.07
C-63	100	10	800	60	320	15	35	3000	-	5.8	1.06
C-65	Tr	20	810	40	390	50	40	3650	-	6.5	0.70
Bodmin											
C-11	100	10	1100	110	600	15	60	3000	-	6.7	0.40
C-12	71	nd	1245	Tr	630	13	45	2950	-	-	0.70
C-13	38	nd	1285	27	740	36	Tr	3470	-	-	-
St. Austell											
C-16	nd	Tr	1235	Tr	368	65	36	4060	-	-	-
C-18	38	Tr	1195	153	403	32	16	3250	-	-	-
C-53	50	Tr	1180	50	300	35	45	4050	-	7.5	0.44
Carnmenellis											
C-20	70	Tr	1280	50	440	Tr	49	2750	-	-	-
C-21	67	Tr	1595	57	878	24	56	3290	-	-	-
C-22	42	10	1540	25	458	20	59	2640	-	7.1	0.72
C-23	63	Tr	1515	32	545	54	34	4270	-	-	-
C-24	Tr	Tr	1525	30	455	37	49	2600	-	-	-
C-25	nd	nd	1660	23	438	35	53	3060	-	-	-
C-26	nd	nd	1480	20	443	80	58	3040	-	-	-
C-27	42	nd	1420	20	610	nd	nd	3230	-	-	-
C-28	63	nd	1405	Tr	448	37	46	2700	-	-	-
C-30	Tr	Tr	1515	60	578	39	49	3330	-	-	-

Appendix I (continued)

Biotite Results

	Zr ppm	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Na %	K %	Ca %
Carnmenellis											
C-32	nd	nd	1370	23	420	26	32	4190	-	-	-
C-34	71	Tr	1175	26	546	39	68	2790	-	-	-
C-36	nd	Tr	1705	33	577	22	31	2900	-	-	-
C-37	46	Tr	1340	35	592	28	36	3690	-	-	-
C-50	60	10	1520	40	390	30	70	2900	-	9.3	0.10
C-51	45	10	1360	15	445	25	60	2900	-	8.9	0.26
C-57	50	nd	70	35	400	20	65	3000	-	8.7	0.25
Lands End											
C-46A	141	13	940	62	216	62	31	1250	-	-	-
C-46B	150	20	970	40	166	65	40	1520	-	-	-
C-49B	145	30	810	45	235	20	40	1950	0.42	5.10	5.3
C-49C	120	Tr	1190	40	190	20	40	1400	0.21	6.7	0.30
C-49D	140	20	620	45	280	40	40	3100	0.20	4.2	0.17
C-49E	95	Tr	440	45	185	15	50	1450	0.40	7.3	0.46
C-49F	95	10	1160	100	175	15	40	1560	0.15	6.3	0.48
C-49G	87	10	1500	40	180	15	45	1500	-	7.6	0.31
C-49H	110	20	1300	50	180	55	45	1900	-	6.7	0.42
C-49I	150	25	620	110	195	30	40	1800	-	3.8	0.54
C-49K	100	10	920	35	260	nd	40	3000	-	6.6	0.48
C-49M	130	5	1110	40	205	25	40	1650	-	6.0	0.48
C-49N	60	Tr	1440	20	160	25	50	1350	-	7.9	0.18
C-49O	100	10	1130	60	180	20	40	1450	-	6.5	0.46
Shap											
Shap 1	Tr	15	510	nd	538	125	120	3420	-	8.8	0.65
Shap 2	79	38	646	30	320	20	135	4050	-	5.4	1.8
Shap 3	70	22	756	30	415	15	135	4550	-	8.6	0.55
Shap 4	80	20	670	30	270	nd	130	3800	0.30	6.8	0.83

Appendix I (continued)

Biotite Results

Criffell-Dalbeattie

	Zr ppm	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Na %	K %	Ca %
D-1	165	20	290	35	345	35	160	2600	-	6.8	0.42
D-2	87	90	440	Tr	320	40	160	2600	-	6.7	0.35
D-4	Tr	120	280	20	280	20	155	2100	0.66	5.8	1.88
D-11	30	50	250	30	215	30	200	2100	-	1.5	3.35
D-14	60	115	500	20	290	20	160	2550	-	7.0	0.28
D-15	85	20	500	Tr	380	25	150	3000	-	5.7	1.62
D-12	45	50	320	25	280	20	120	2800	-	2.3	3.10
D-6	120	20	460	25	545	20	140	4450	-	-	-
D-8	165	35	300	75	565	20	110	4700	-	3.6	0.39
D-9	95	45	720	30	445	30	140	3500	0.34	5.9	1.54
D-10	70	35	610	20	410	50	135	3250	-	6.7	1.36
D-13	75	40	850	35	480	20	130	4100	-	8.1	0.77

Etive Complex

Allt na Lairige

E-1	115	200	250	25	445	20	105	3950	-	3.9	1.56
E-2	145	80	320	35	575	40	130	3900	-	5.4	1.64
E-3	40	65	310	30	540	35	140	3800	-	-	-

Ballachulish

E-19	nd	110	230	30	265	35	105	2400	-	4.0	2.48
E-20	70	190	260	30	280	50	105	2250	-	7.1	1.16
E-22	100	130	220	35	235	20	115	2100	-	4.5	2.14
E-21	120	280	390	50	370	50	105	2900	-	5.2	1.26

Cruachan

E-7	Tr	95	250	25	375	25	50	2000	-	7.9	0.74
E-8	65	65	270	30	170	20	40	2000	-	8.3	0.70
E-12	35	60	170	30	305	25	115	1850	-	6.8	1.34

Appendix I (continued)

Biotite Results

	Zr ppm	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Na %	K %	Ca %
Cruachan											
E-13	50	80	210	60	320	25	85	1800	-	9.7	1.04
E-14	Tr	450	60	25	280	70	150	1700	-		3.54
E-15	100	365	300	15	260	75	100	1550	-	5.2	1.78
E-9	120	55	210	nd	445	45	40	2050	-	7.8	0.49
E-16	100	90	170	30	430	30	75	3200	-	4.8	1.82
E-23A	115	75	395	25	360	nd	150	2850	-	5.2	1.73
E-24	45	250	180	15	300	30	100	1400	-	3.9	2.02
Strontian											
S-16	158	60	376	36	545	15	130	3500	0.44	4.7	1.34
S-13	62	230	150	36	295	60	180	2200	-	-	3.95
S-15	40	100	250	Tr	320	30	205	2300	-	7.4	0.22
S-3A	102	132	200	16	40	30	116	2460	-	-	4.2
S-4	nd	55	210	16	389	47	200	2120	-	5.9	2.5
S-5	45	70	470	15	240	20	155	2400	-	-	-
S-6	240	50	166	Tr	445	45	200	2440	-	-	-
S-7	63	80	210	20	295	40	200	2250	-	7.0	0.29
S-8	nd	32	221		400	39	178	2090	-	-	-
S-10	120	35	290	25	460	65	35	4350	-	6.6	0.97
S-11	60	205	240	25	240	20	155	2100	0.87	4.7	1.94
S-12	45	25	290	20	290	15	165	2200	-	8.6	0.57
S-14	57	23	360	20	260	15	155	2650	-	8.8	0.65
Foyers											
F-1	50	75	200	25	275	15	60	3450	-	5.1	1.86
F-4A	65	80	160	30	345	20	35	3200	-	7.9	0.83
F-4B	65	35	190	35	295	40	50	3600	-	4.9	1.18
F-5	100	20	260	35	340	30	40	3550	-	7.4	0.62
F-8	Tr	60	180	25	350	nd	40	3300	-	7.9	0.79

Appendix I (continued)

Biotite Results

	Zr ppm	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Na %	K %	Ca %
Foyers											
F-9	60	60	130	30	325	30	30	3350	-	5.6	1.29
F-2	Tr	40	240	25	280	20	65	2950	-	6.6	1.63
F-3	110	50	180	20	295	60	65	3300	-	1.1	3.36
F-7	50	50	200	20	320	40	70	3050	-	4.0	1.17
F-10	35	50	100	20	455	25	40	3600	-	7.3	1.08
Aberdeen											
A-1	Tr	10	560	40	420	40	60	-	-	9.2	0.19
A-2	165	10	370	35	220	30	25	2050	-	7.5	0.15
A-3	185	10	360	35	240	5	25	2250	-	7.2	0.17
A-4	215	20	290	35	250	20	20	1450	0.10	6.3	0.41
A-7	50	25	350	25	390	35	20	2100	-	6.1	0.47
A-9A	35	45	380	25	420	55	120	4400	-	6.4	0.76
A-10	nd	60	430	25	470	35	115	3450	-	5.3	0.80
A-5	110	40	350	25	565	20	70	4300	-	5.1	0.62
A-6	115	30	430	35	600	20	50	4800	-	5.9	0.62
A-21	200	35	380	30	460	15	80	3750	-	5.1	0.76
A-19	40	25	380	20	320	20	30	1950	-	4.9	0.30
Peterhead											
A-15	40	15	200	45	260	20	30	3350	-	6.7	0.18
A-16	175	Tr	670	25	355	20	55	2300	-	6.5	0.10
Fraserburgh											
A-17	50	nd	470	25	280	15	40	2600	-	7.0	0.25
A-18	80	10	540	15	315	20	40	2700	-	7.0	0.23

Appendix I (continued)

Biotite Results

Strathdearn

	Zr ppm	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Mn ppm	Na %	K %	Ca %
A-24	Tr	20	230	30	275	15	50	5100		5.8	0.44
A-25	nd	20	440	15	310	20	40	3350	-	6.5	0.20

Appendix I (continued)

Muscovite Results

All samples are at least 98% pure, the remaining 2% being largely feldspar with minor biotite.

	Zr	Sr	Rb	Pb	Zn	Cu	Ni	Mn
Dartmoor								
C-59	nd	Tr	2720	20	325	30	35	4480
Bodmin								
C-11	33	11	1920	209	150	310	10	680
C-12	69	18	1580	33	130	12	9	580
C-13	40	10	1750	40	125	10	35	655
St. Austell								
C-55	nd	35	5700	Tr	75	35	40	1835
Carnmenellis								
C-20	95	18	11800	27	125	160	16	680
C-23	40	47	1640	27	100	62	21	682
C-25	69	42	1460	55	85	29	18	520
C-26	56	12	1610	Tr	91	79	19	545
C-27	69	48	1340	100	94	70	nd	350
C-28	89	19	1980	45	99	34	nd	600
C-30	Tr	20	2180	30	130	36	27	945
C-32	79	33	1960	40	214	24	22	765
C-34	76	50	1430	70	91	114	18	575
C-36	63	Tr	2420	Tr	168	nd	33	1100
C-37	76	19	1810	45	122	Tr	21	1035
Lands End								
C-48A	nd	12	1950	27	123	41	90	415
C-44	nd	nd	5060	Tr	217	56	66	280
Cligga Head								
C-58	nd	40	2170	45	180	15	20	2080

Appendix I (continued)

Muscovite Results

Weardale

	Zr	Sr	Rb	Pb	Zn	Cu	Ni	Mn
W-1	115	40	1160	Tr	150	35	15	735
W-2	40	25	1360	20	340	10	25	1960
W-3	nd	20	1620	Tr	310	15	20	1420
W-4	55	20	1090	30	400	35	15	1145
W-5	nd	10	1560	Tr	320	15	20	1600
W-6	55	45	1010	40	180	15	20	1050
W-7	Tr	35	990	25	160	25	15	1050
W-8	55	40	900	Tr	170	25	10	740

Appendix II

The Determination of Sodium and Potassium in Rocks and Minerals using the Eel Flame Photometer

After E.A. Vincent

Department of Geology and Mineralogy, Oxford.

Preparation of Standard Solutions

For Na_2O: Exactly 0.2162 g A.R. sodium oxalate, previously dried at 105°C is weighed out on a watch-glass, dissolved in distilled water and made up to 500 ml in a standard flask.

For K_2O: Exactly 0.2146 g of A.R. potassium nitrate is weighed out and dissolved in the same way.

(These two solutions are kept as stock solutions in polythene bottles).

Ammonium carbonate: 10 g powdered A.R. ammonium carbonate is dissolved in 50 ml distilled water plus 50 ml concentrated ammonia solution. Do not heat.

The solution is kept in a polythene bottle.

Working standards

Two calibration curves are available for the photometer - one for concentrations of Na_2O and K_2O up to 12 γ/ml and one for concentrations up to 24 γ/ml, and standards of these two limiting concentrations are required.

For the 24 γ/ml standards, run 30.0 ml each of the standard sodium oxalate and potassium nitrate stock solutions from burettes into a 250 ml standard flask. Dilute somewhat, add 2.5 ml of the ammonium carbonate solution (from a graduated pipette), make up to the mark, and mix thoroughly.

For the 12 γ/ml standard, proceed in the same way, but take 15.0 ml of each of the stock alkali solutions.

24 γ/ml and 12 γ/ml standards, ready for use, are stored also in polythene bottles.

Preparation of sample

Weigh accurately into a platinum crucible an appropriate amount of the finely ground sample. About 100 mg for an acid rock, 150 - 200 mg for a basic rock or ferromagnesian mineral, 50 mg. for an alkali feldspar, are usually about right.

Add 2 ml 50% H_2SO_4 and 4 ml HF (from the palua scoop). Heat, uncovered, on the electric crucible heater at about 150°C to begin with, and when fumes of SO_3 begin to appear, cautiously increase the temperature and evaporate to dryness.

Cool, add one drop 50% H_2SO_4 and half fill the crucible with distilled water. Stand on the waterbath, with occasional agitation, for at least one hour, until all soluble material has gone into solution. Add more water from time to time if necessary.

Transfer the contents of the crucible, without loss, through a funnel into (generally) a 250 ml standard flask, rinsing the crucible several times with distilled water from a plastic wash-bottle.

Add distilled water until the flask is about two-thirds full; then add 2.5 ml of ammonium carbonate solution (1 ml for every 100 ml of final solution) from a graduated pipette, swirl the solution gently, and make up to the mark. Shake thoroughly, and allow to stand 5 - 10 minutes. This will precipitate Al, Fe, Ti, Ca, Mg, etc., which would otherwise interfere in the determination.

Filter the solution through a dry No. 41 paper in a dry funnel into one of the small dry beakers for the photometer. Reject the first three beakerfuls and reseve the next for measurement.

Measurement on the photometer

Light the gas flame, turn on the compressed air and adjust the air valve on the side of the instrument until the pressure gauge reads exactly 10 lbs. per square inch. Unclamp the galvanometer.

Place a small beaker of distilled water under the capillary intake, and adjust the gas control valve on the side of the instrument until the flame just breaks into ten separate small blue cones. Close the photometer lid, having first checked that the appropriate filter is in position.

Take the appropriate working standard solution (24γ/ml or 12γ/ml) in another small beaker, and place beneath the capillary intake. Adjust the potentiometer control (front of instrument) until the galvanometer reads about 100. Then spray distilled water and adjust the galvanometer index to zero, using the zero control on the side of the instrument. Spray the standard again, and this time adjust the potentiometer so that the galvanometer reads exactly 100. Spray distilled water and check the zero.

Then spray the sample solution, and read the galvanometer. Take three separate readings of the galvanometer for the sample solution. Return the potentiometer to zero, and repeat the whole procedure again.

Read off on the calibration curves the concentrations of Na_2O and K_2O in the sample solution ($1\gamma = 0.000001$ g) $= 10^{-6}$ gm).

Before leaving the photometer, spray plenty of distilled water to clean the burner; return the potentiometer to zero; clamp the galvanometer and see that gas and compressed air supplies are turned off properly.