Measurement of the modal composition of a granitic rock powder by point-counting, infra-red spectroscopy, and X-ray diffaction

By P. M. D. BRADSHAW

Department of Geology, University of Durham[1]

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Summary. A rapid method for determining the mode of a four-component powder (microcline, orthoclase, plagioclase, and quartz) was sought to aid the interpretation of geochemical results. An accuracy of about ±5 % (absolute) was required. Three methods were tried: point counting proved too long as well as destroying the sample; infra-red spectroscopy was not sufficiently accurate for this particular type of rock powder; X-ray diffraction proved the most rapid and, although less accurate than point counting, was within acceptable limits and had the advantage of giving additional information about the composition of the feldspars.

TO aid in a recent geochemical investigation (Bradshaw, 1965) an estimate of the concentration of the minerals present in a rock powder containing only microcline, orthoclase, plagioclase, and quartz was required. A method of determining the concentration of the minerals directly (the mode) was considered quicker and superior to a recalculation from a chemical analysis (the norm). Point-counting, infra-red spectroscopy, and X-ray diffraction were all used quantitatively: the latter proved the most useful.

The rock powders were all of granitic composition and had previously been crushed and sieved ready for chemical analysis. A Cook magnetic separator was used to remove all the magnetic minerals, whose weight per cent could easily be determined, leaving a powder that was at least 98 % pure feldspar plus quartz.

Point-counting

To alleviate the problem of counting a coarse-grain porphyritic rock, 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 these were first stained.

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[1] Present address: Applied Geochemistry Section, Imperial College, London.

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 g of the sieved homogeneous powder (between 58 and 155 mesh) were placed in the bottom of a tall, 200 ml teflon beaker and completely covered with hydrofluoric acid. After 2 minutes a gentle stream of cold water was directed into the beaker and allowed to run for 4 to 5 min, the excess water spilling over the edge. Care was taken to ensure that the water pressure was not strong enough to wash 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 which was used to hold them while they were 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. No standards of a suitable size could be found to check the accuracy of this method but the precision was found to be about 2 %. However, the method is time consuming (about 45 minutes per sample), destroys the sample for 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 that did not incur 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 to natural silicates as a qualitative method (Launder, 1952; Laves and Hafner, 1956 and 1962; Hafner and Laves, 1957), and a quantitative method (Hunt and Turner, 1953; Lyon *et al.*, 1959). A total of 51 infra-red curves of standard samples were run in order to establish the accuracy of the quantitative method.

Technique. The standard procedure for making potassium bromide discs was employed. The original powder was ground in a tungsten-carbide vial using a spex mixing mill, sieved to below 150 mesh and about 5 g ground for a further 30 minutes. This grinding process was found to be just sufficient to reduce the grain size below 5 μ, the particle size above which refraction around the grains starts causing poor peak resolution and a high background. Sample and potassium bromide were mixed in the proportion 1 : 3 and put in a stainless steel die and pressed under vacuum for 10 minutes at 12 tons giving a sample concentration of 0·82 mg/cm^2. 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 μ at 2 minutes per μ using slit programme number 10 at normal gain.

A series of artificial mixes, using only 2 of the 4 end members at a time, were made for the initial calibration and several mixes consisting of 3 end members (orthoclase, quartz, and plagioclase) were made to give further control.

Results. Fig. 1 shows the traces of the pure end members, microcline, orthoclase, plagioclase (oligoclase), and quartz. Initially the results were determined using the same method and peaks as Lyon *et al.* (1959), i.e. the per cent transmission of the 12·45 μ and 14·41 μ peaks for quartz, 13·48 μ for oligoclase, and 13·76 μ for microcline and orthoclase. These peaks, however, were found to be unsatisfactory and gave poor results. The quartz peak at 12·45 μ disappears if quartz falls below 50 % of the total, and the plot of per cent transmission of the 14·4 μ peak as per cent quartz gave erratic results and errors of 10 % (absolute) were common. The height of the oligoclase peak (13·48 μ), and therefore the optical density, was found to vary with the high and low temperature

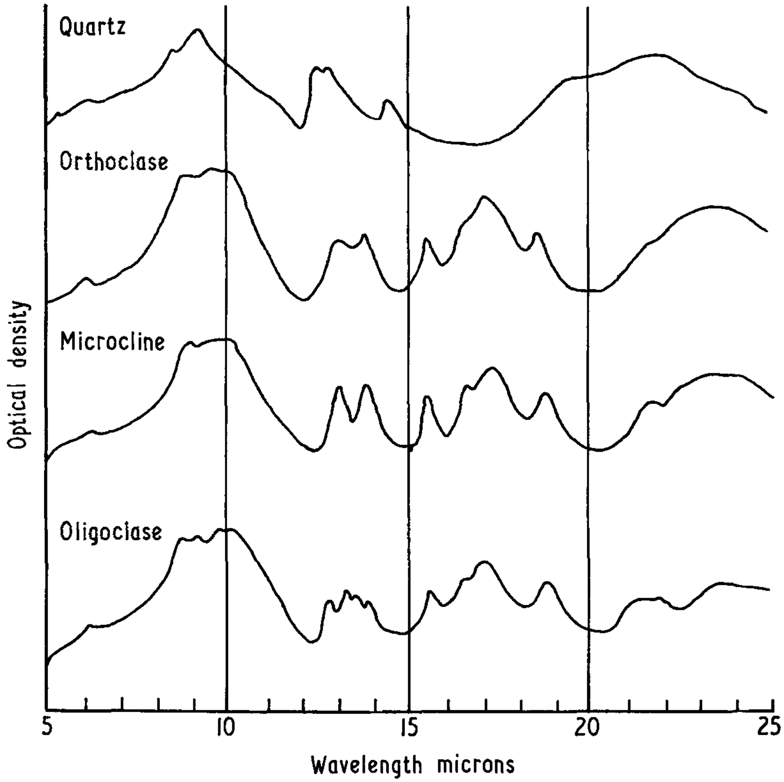

FIG. 1. Infra-red curves for quartz, orthoclase, microcline, and oligoclase.

forms as shown by the heating experiments of Laves and Hafner (1956); this applies to all plagioclase peaks. It was found also that the optical density of all the K-feldspar peaks increases with obliquity independent of the K-feldspar concentration; this observation is also reported by Liese (1964) and by Hafner and Laves (1957) and can be seen by comparing the traces of microcline and orthoclase (fig. 1). It appears therefore, that unless the K-feldspar is known to be either all microcline or all orthoclase, and the plagioclase is known to be either all the high or all low form, a precise quantitative determination of K-feldspar and plagioclase concentration based on optical density is impossible. Even if these factors are known, the peaks are all relatively small and even under ideal conditions the precision will be low. As most of the rocks examined during the present investigation are known to have a mixture of orthoclase and microcline the application of this technique was not feasible.

Especially after considering the errors shown by Lyon *et al.* (1959), in their analysis of G–1 it was decided to develop the X-ray diffraction technique in preference to the infra-red. An average of their results showed an absolute percentage error of 8·3 % for quartz and plagioclase and 5·5 % for K-feldspar.

Analysis time was about 1 hour per sample.

X-ray diffraction

The use of the intensity of X-ray diffraction lines as a quantitative measure of the minerals present in a powder was suggested as long ago as 1919 by Hall. More recently Klug and Alexander (1954) gave a review of this method and showed that an accuracy of ±5 % of the amount of mineral present was quite possible for some mixes; Tennant and Berger (1957), Diebold *et al.* (1963), and Otalora (1963, personal communication) have also used this technique, and all report a similar accuracy. However, all the workers seem to have applied this method to carbonates or clay-rich specimens, no recorded instances of the determining of quartz and feldspar concentrates was found.

Technique. Standard curves were constructed using the same standard mixes as were employed during the infra-red investigation. Three separate cavity mounts were scanned in turn using a Philips PW1010 generator and PW1050 goniometer, 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 and the results plotted as shown in fig. 2. Using a Cu-$K\alpha$ radiation at 40 Kv and 20 mA with discrimination, rate meter 4, scan speed $\frac{1}{2}^\circ$ (2θ) per min, and chart speed times 20, a background of about 5 chart divisions was found while the most intense peak did not generally exceed the limits of the chart.

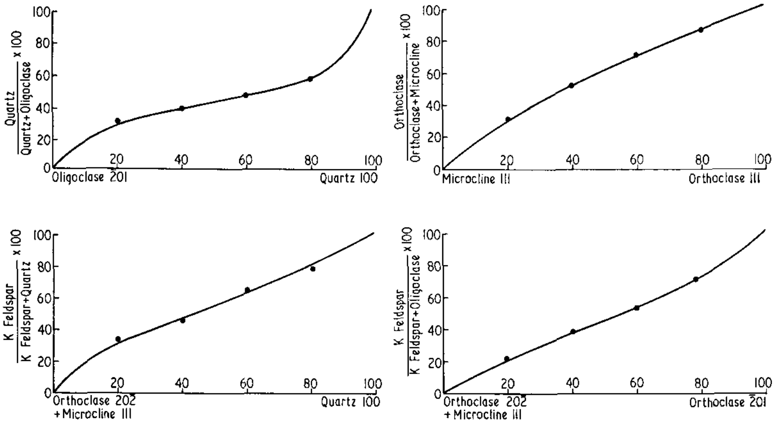

FIG. 2. Relative intensity of quartz, orthoclase, microcline, and plagioclase X-ray diffraction peaks.

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 heights of the plagioclase $\bar{2}01$, quartz 100, and orthoclase $20\bar{2}$ plus microcline 111 gave the plagioclase : quartz : feldspar ratio, while the heights of the orthoclase 111 and microcline 111 gave the orthoclase : microcline ratio. It was possible to measure the obliquity of the K-feldspar at the same time by the separation of the orthoclase 111 and microcline 111 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 fig. 2 the K-feldspar : oligoclase, oligoclase : quartz and quartz : K-feldspar ratios are determined, giving 3 equations in 3 unknowns from which the percentages of K-feldspar, oligoclase, and quartz can be determined. From the other graph the microcline : orthoclase ratio can also be calculated. Table I shows the determined values of several artificial mixes whose known compositions are shown in the right-hand column. It can be seen from the table that all the results fall within ±6 % (absolute) and that the majority are considerably better. A higher precision can probably be obtained by rotating the specimen, taking the average of 10 rather than 3 determinations of each peak, measuring the area under the curve rather than peak height, or using an internal standard to obtain a straight line rather than curved graphs. However, the results were considered sufficiently accurate for the interpretation of the geochemical data involved and it was thought that the extra time involved for greater precision was not warranted. Using the method described, analysis took about 35 minutes per sample.

TABLE I. Mineral percentages determined in several artificial mixes by X-ray diffraction

Artificial mix		X-ray diffraction determination		Difference of average
Quartz	20 %	23 %	25 %	4 %
Orthoclase	50	50	47	1·5
Oligoclase	30	26	28	3
Quartz	10	15	17	6
Orthoclase	40	34	38	4
Oligoclase	50	50	47	1·5
Quartz	33	39	38	5·5
Orthoclase	33	33	33	0
Oligoclase	33	27	28	5·5

Conclusion

Infra-red spectroscopy was found to be too slow and have an unacceptably low accuracy to be of use during the present study. X-ray diffraction and point counting require about the same time per sample but X-ray diffraction has the added advantage of analysing a larger proportion of the sample, does not destroy the sample, and can distinguish quantitatively between microcline and orthoclase as well as measure the An composition of the plagioclase. Although the precision and most probably the accuracy of the X-ray method used was lower than that of point counting, it was still within acceptable limits and therefore was considered superior.

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Erratum

THE author regrets that he only found an error in the wording on fig. 2 (p. 98) when the paper was in proof. The bottom left-hand graph should read quartz on the left, and orthoclase+microcline on the right; the bottom right-hand graph should read oligoclase (not orthoclase) on the left, and orthoclase+microcline on the right.