

Modal analyses of granitoids by quantitative X-ray diffraction

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ABSTRACT

Modal proportions of quartz, plagioclase, perthite, and/or orthoclase are determined in artificial mixtures (presumed to simulate granitoids) and in actual granitoids by X-ray diffraction. This procedure utilizes the ubiquitous presence of quartz in all samples as an internal standard. Selected peak ratios along with the total volume fraction of these minerals and the predetermined constants can be used to calculate the volume fraction of various minerals.

The percentage relative error for this technique, excluding counting statistics, has a standard deviation of 7%. X-ray diffraction analysis is capable of routine, rapid modal analysis, provided the preparation and analysis of the sample is carefully controlled. With minor modification, this method can be adapted to other rock types.

INTRODUCTION

Modal analyses of granitoids are important for the following reasons: (1) for classification and comparison with other rocks, (2) for preliminary estimates of pressure and temperature of crystallization utilizing Q-An-Ab-Or phase relations and petrography, (3) for preliminary characterization of tectonic environment of the rocks (Bowden et al., 1984). The standard procedure for modal analyses is point counting of minerals in thin section (Chayes, 1956). The point-counting method has several drawbacks: (1) it is time consuming and tedious, (2) it cannot be used for volcanic or very fine grained rocks, (3) in crystalline rocks as the average grain size increases, obtaining representative modal analyses requires point counting of an increasing number of standard-size thin sections, and (4) error is introduced owing to misidentification of minerals. These factors can lead to serious errors in modal analyses of granitoids.

X-ray diffraction (XRD) has been routinely used to identify the mineral constituents of samples. Many methods have been developed for quantitative XRD, some using external standards (Copeland and Bragg, 1958), others using internal standards (see Klug and Alexander, 1954), and some that eliminate standards (Zevin, 1977; Geohner, 1982; see also Brindley (1980) for discussion of these methods). Geohner (1982) discussed the principles of quantitative analysis of a mixture which can be easily adapted for routine, rapid modal analyses of geologic samples. Pawloski (1985) utilized this procedure to quantify (in weight percent) minerals present in samples of Tertiary volcanic tuffs and Tertiary-Quaternary alluvium from the Nevada Test Site. Pawloski (1985) quantified the feldspars as a single group and did not distinguish between the different feldspars. For modal analyses of granitoids it is crucial to distinguish between the different feldspars. We use a version of Geohner's method to

quantify (volume percent) major minerals in granitoids. The method can (1) distinguish between plagioclase and alkali feldspar and (2) distinguish between orthoclase and microcline and thereby give modal proportions of quartz, perthite, orthoclase, and plagioclase in granitoids. The principles of the technique can be used to quantify any type of rock by following a similar procedure modified to suit one's needs.

BASIC PRINCIPLES AND CALCULATIONS

The basic equation utilized is (Klug and Alexander, 1954)

$$I_{i,p} = \frac{(K_{i,p})(V_p)}{m}, \quad (1)$$

where $I_{i,p}$ = diffraction intensity of peak i , for component p in the mixture; $K_{i,p}$ = a constant of peak i , for component p (this constant also depends on the machine characteristics); V_p = volume fraction of component p in the mixture; and m = average attenuation coefficient of the mixture (m is characteristic of a specific sample being analyzed and will change if the proportion of any component is changed).

For a multicomponent mixture with n components, we can write equations of the type (using Eq. 1),

$$I_{i,a}/I_{j,b} = (K_{i,a})(V_a)/(K_{j,b})(V_b), \quad (2)$$

where a and b = components and i and j = peak positions. If we can recognize at least n different peak positions for this mixture then, we can write $(n - 1)$ such equations. For peaks that are not unique to a single component, i.e., have contributions from two or more components, equations like Equation 2 will be additive. If we calibrate the X-ray diffractometer for K ratios using key reflections, we can then obtain volume ratios for the components in the unknown.

In an unknown, we have another constraint:

$$\sum_{x=1}^n V_x = C, \quad (3)$$

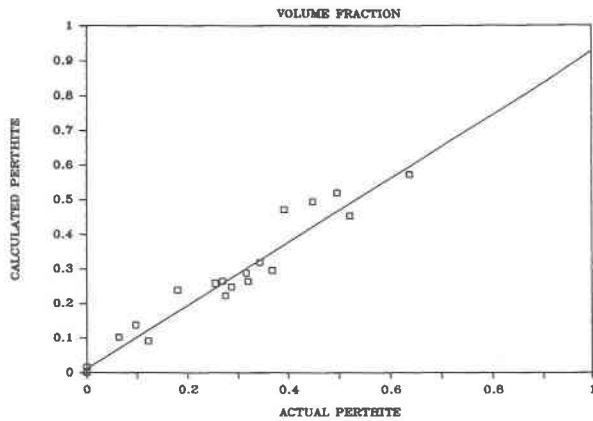


Fig. 1. Calculated vs. actual perthite for artificially prepared mixtures ($y = 0.93x + 0.012$; $r = 0.975$).

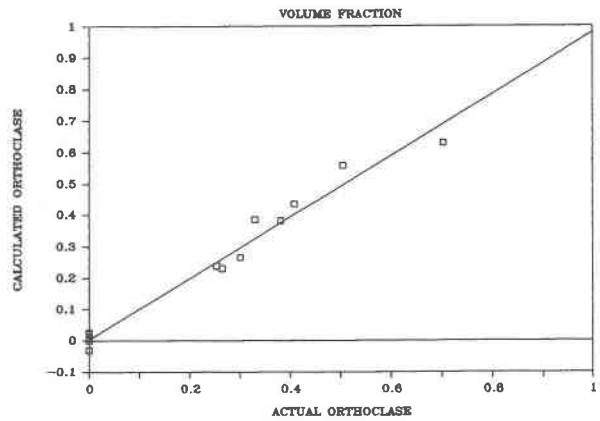


Fig. 2. Calculated vs. actual orthoclase for artificially prepared mixtures ($y = 0.98x + 0.003$; $r = 0.991$).

where C = total volume fraction of n components analyzed and V_x = volume fraction of component x .

We now have n components to be quantified and n equations [($n - 1$) of the type of Eq. 2 + Eq. 3]. We can therefore uniquely determine the volume fractions of the components under consideration.

In granitoids, the minerals of interest—quartz, plagioclase, orthoclase, and/or, perthite—constitute more than 90% by volume of the rock. Modal analyses of these minerals should represent the granitoids satisfactorily. For XRD analyses, these minerals represent the following components: quartz (q), plagioclase (p), orthoclase (o), albite exsolved in perthite (a), and microcline (host) of the perthite (m). Table 1 lists the 2θ angles used with the components represented at these angles. This results in the following equations:

$$\frac{I_{2,p+a}}{I_{1,q}} = \frac{(K_{2,p})(V_p)}{(K_{1,q})(V_q)} + \frac{(K_{2,a})(V_a)}{(K_{1,q})(V_q)} \quad (4)$$

We make the assumption that the $K_{2,p}$ and $K_{2,a}$ constants will be the same. This assumption seems justified considering that plagioclase composition in granitoids is usually between albite and andesine; therefore the characteristics of the two components ought to be similar. Equation 4 therefore reduces to

$$\frac{I_{2,p+a}}{I_{1,q}} = \frac{(K_{2,p})(V_p + V_a)}{(K_{1,q})(V_q)} \quad (4')$$

We also have

$$\frac{I_{3,o+m}}{I_{1,q}} = \frac{(K_{3,o})(V_o)}{(K_{1,q})(V_q)} + \frac{(K_{3,m})(V_m)}{(K_{1,q})(V_q)} \quad (5)$$

and

$$\frac{I_{4,m}}{I_{1,q}} = \frac{(K_{4,m})(V_m)}{(K_{1,q})(V_q)} \quad (6)$$

Finally we have,

$$V_o + V_m + V_a + V_p + V_q = C, \quad (7)$$

where V_x = volume fraction of component x and C = the total volume fraction (approximately = 0.95, or this can be estimated from thin section or hand sample).

APPLICATION OF THE TECHNIQUE

Determination of K constants

We made artificial mixtures with varying proportions of these minerals. The weight of each mineral in the mixture is known, from which the volume fraction of each mineral can be calculated. These standards were X-rayed, and the intensity ratio ($I_{\text{component}}/I_{\text{quartz}}$) determined and plotted against volume-fraction ratio ($V_{\text{component}}/V_{\text{quartz}}$). A calibration curve for each component pair was obtained by a linear least-squares fit of the data, and the slope of the line was taken as the K ratio ($K_{i,\text{component}}/K_{i,\text{quartz}}$). These constants are listed in Table 2. The experimental procedure for these standards is discussed in the next section.

Quantifying the unknown sample

From Equations 4', 5, 6, 7 and Table 2, we have for an unknown sample that has been X-rayed, five unknowns (V_a , V_m , V_o , V_p , V_q) and only four equations. This cannot be solved for the unknowns. If we make the assumption that in the perthite, the exsolved albite component is 30%, then we have

$$V_m = (2.333)V_a \quad (8)$$

This assumption is approximately valid for most granitoids (Deer et al., 1963). Alternatively, the perthite composition could be determined by some other method. We can now solve for the volume fractions of the minerals in the sample.

EXPERIMENTAL PROCEDURE

Preparation of the standard mixtures was done using pure samples of quartz, orthoclase, perthite, and oligoclase. The purity of these minerals was checked by X-raying them individually. The pure minerals were sieved to less than 30 μm before the weighing to provide a practical optimum size for X-ray analysis. Although finer-grain sizes may be preferred (Klug and Alex-

TABLE 1. Characteristic peak positions (2θ) used to identify and quantify mineral components

Peak	2θ	Components represented
1	20.82	Quartz
2	21.95–22.0	Plagioclase + exsolved albite in perthite
3	27.0–27.1	Orthoclase + microcline of perthite
4	27.40–27.45	Microcline of perthite

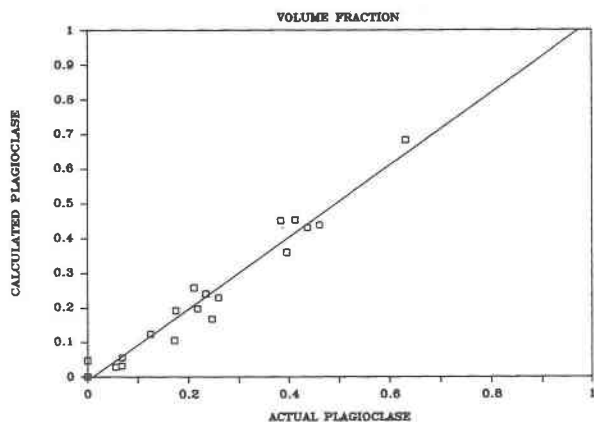


Fig. 3. Calculated vs. actual plagioclase for artificially prepared mixtures ($y = 1.04x - 0.011$; $r = 0.982$).

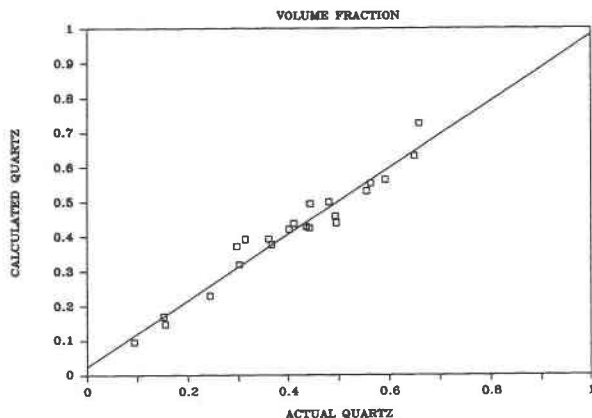


Fig. 4. Calculated vs. actual quartz for artificially prepared mixtures ($y = 0.96x + 0.025$; $r = 0.974$).

ander, 1954), preparation times for these grain sizes increase considerably. The samples were thoroughly mixed and sifted onto Vaseline-coated slides to provide random mounts. Over 200 independent analyses of carbonate (calcite and dolomite) composition by one of the authors (Cooke) verifies the randomness and reproducibility of this slide-preparation technique. A 0.979 correlation coefficient was obtained in comparing X-ray-determined carbonate composition with weight loss on acid digestion. Possible problems in reproducing peak intensities caused by lack of infinite thickness or absorption of X-rays by the Vaseline binder are eliminated by the ratio technique that we employ for calculation.

Duplicates of selected samples were prepared and mounted to check that mixing was thorough and randomness obtained. All samples were run on a Philips Norelco X-ray diffraction unit equipped with a Cu-X-ray tube and Ni filter. X-ray diffractograms were obtained from 18°–30° 2θ range with operating conditions of 45 keV, 30 mA, 0.25°/min scan rates, and fine slit settings. The quartz peak (100) at 20.82° 2θ was used as an internal standard to calibrate the peak positions. The required peaks were located and their intensities tabulated.

ACCURACY OF THE METHOD

Modal analyses of 22 samples (10 of these we used in *K* constant determinations) were determined by the method developed above. The comparisons of actual versus calculated analyses for each mineral are plotted in Figures 1 through 4 along with a linear regression line and the correlation coefficient. Deviation of the regression lines from slope = 1 and *y*-intercept = 0 illustrates the potential for further refinement of the *K* constants by running more standards.

The accuracy of this technique can be assessed by ex-

amining the percentage relative errors of the samples. The parameter utilized is

$$[(V_a - V_c)/V_a] \times 100,$$

where *V_a* is the actual volume fraction and *V_c* is the calculated volume fraction.

Sources of error include grain size, slide-preparation technique, accuracy of *K* constants, and machine parameters. One of the machine parameters, the counting statistics, will increase the percentage relative errors of the component analyzed as the actual volume fraction of the component decreases. This effect can be reduced or eliminated by slower scanning or by fixed-count accumulation of data at each selected peak position. Table 3 shows the effect of counting statistics, reported as the standard deviation of percentage relative errors for the actual values with specific ranges. The ultimate accuracy of this technique, excluding counting statistics, has a standard deviation of 7%. For the range of compositions that we prepared, the detection limit was not reached. At best, we can estimate the detection limit to be less than 2–3% by volume. With adjustments to the scanning rates to improve counting statistics, detection limits on the order of 1% by volume should be achievable. These limits should be suitable for modal analyses of granitoids.

APPLICATION OF TECHNIQUE TO NATURAL GRANITOIDS

We have demonstrated that the technique described is applicable to artificially prepared mixtures containing

TABLE 2. Determined values of *K* constants

<i>K</i> _{component} / <i>K</i> _{quartz}	Values
<i>K</i> _{2,p} / <i>K</i> _{1,q}	0.3700
<i>K</i> _{3,o} / <i>K</i> _{1,q}	0.3500
<i>K</i> _{3,m} / <i>K</i> _{1,q}	0.4000
<i>K</i> _{4,m} / <i>K</i> _{1,q}	1.9000

TABLE 3. Statistical analyses of artificially prepared mixtures

<i>V_a</i> of mineral analyzed	Standard deviation (of % relative errors)
>0.40	6.8%
0.30–0.40	12.0%
0.20–0.30	12.5%
0.10–0.20	17.7%
<0.10	37.0%

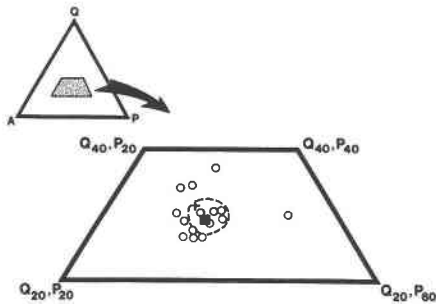


Fig. 5. Quartz (Q)–alkali feldspar (A)–plagioclase (P) ternary diagram comparing point-counted data to quantitative XRD data for USGS Standard G-1. Symbols used: dashed line = range for point-counted data taken from Chayes (1951); solid square = mean value of point-counted data; open circle = XRD modal data; plus sign = mean value of XRD data.

minerals commonly occurring in granitoids. The critical question is whether the procedure is applicable to natural rock specimens, in our case granitoids. We determined the modes of five granitoids by using both the traditional point counting of thin sections and polished rock slabs and the quantitative XRD procedure outlined in this paper. The five granitoids analyzed are (1) USGS standard G-1, (2) Troy Granite, Arbuckle Mountains, Oklahoma, (3) Tishomingo Granite, Arbuckle Mountains, Oklahoma, (4) unnamed granodiorite, Arbuckle Mountains, Oklahoma, and (5) Blue River Gneiss, Arbuckle Mountains Oklahoma. We shall briefly describe the petrography of each granitoid and discuss the results.

USGS granite standard, G-1, is available in powder form and used in many laboratories. G-1 is the fine-grained Westerly granite from Rhode Island. Quartz, alkali-feldspar, and plagioclase constitute approximately 90% of the rock. Biotite, muscovite, opaques, and accessory minerals make up the rest (Chayes, 1950, 1951). We use the point-counting data published in USGS Bulletin 980 for the G-1 standard. For XRD analyses we ran 15 samples, and the comparison between point-counting and quantitative XRD is shown in Figure 5 and Table 4.

Troy Granite is fine- to medium-grained hypidiomorphic equigranular with quartz, perthite, and plagioclase constituting approximately 90% of the rock. Biotite, occasional hornblende, opaques (mainly magnetite), sphene, apatite, zircon, and secondary minerals occur in minor proportions. Seven standard-size thin-sections from different localities were point-counted (500 points per thin section). One of the difficulties encountered was distinguishing between plagioclase and alkali feldspar when both occur untwinned, plagioclase is unzoned, and alkali feldspar does not display obvious exsolution. For XRD, 14 different samples were ground and analyzed. The comparison between the point-counting and the XRD analyses is shown in Table 4.

Tishomingo Granite is coarse-grained hypidiomorphic inequigranular displaying large euhedral porphyritic perthites [up to 2 in. (5 cm) long]. Quartz, perthite, and plagioclase constitute approximately 85–90% of the rock. Minor minerals are similar to those found in Troy Granite except sphene occurs in a higher proportion (approx. 2–5%). Point counting of thin sections alone is not adequate owing to the porphyritic nature of perthites. This required a composite point counting of both thin sections and a polished rock slab [approx. 4 × 6 in. (10 × 15 cm)] from which the thin section was prepared. Seven such composites, each from a different locality, were point-counted (500 points). For XRD analysis, 18 different samples were ground and analyzed. The comparison between the point-counting and the XRD analyses is shown in Table 4.

The unnamed granodiorite is a medium-grained hypidiomorphic equigranular rock with quartz, plagioclase, perthite, and occasional pure microcline constituting approximately 70–80% of the rock. Hornblende and biotite add another 10–15%, and the accessories make up the remaining 2–5%. Five standard-size thin sections from various localities were point-counted (500 points each). For XRD, nine samples from different localities were ground and analyzed; the results in comparison to point counting are shown in Table 4.

Blue River Gneiss is a moderately variable rock in the

TABLE 4. Comparison between point-counting and quantitative XRD techniques of natural granitoids

Sample	Point counting			Quantitative XRD				
	No. of samples	Quartz	Alkali feldspar	Plagioclase	No. of samples	Quartz	Alkali feldspar	Plagioclase
Sample G-1	16	29.17	37.56	33.28	15	31.78	37.41	32.03
Troy Granite	6	1.51	1.48	1.41	3.55	4.05	3.87	
		27.77	44.37	27.87	28.72	42.57	28.71	
Tishomingo Granite	7	6.00	11.41	12.04	8.67	12.58	15.36	
		31.31	38.77	29.90	27.61	37.56	34.84	
Unnamed granodiorite	5	6.84	6.18	9.09	7.04	9.31	12.34	
		17.26	16.14	66.60	20.69	11.39	67.92	
Blue River Gneiss— A (felsic component)	5	5.61	11.90	6.31	6.94	8.03	11.77	
		30.36	37.52	32.12	29.35	37.87	32.77	
Blue River Gneiss— B (mafic component)	3	7.83	5.23	7.89	4.70	12.10	13.48	
		17.60	9.23	73.17	16.66	6.86	76.50	
		4.16	9.40	6.50	7.94	5.47	10.84	

Note: First line of each pair of lines gives the mean; the second line gives the standard deviation.

field, and specimens reported here occur as coarsely intermixed gneiss displaying both leucocratic and melanocratic members. Both members of the gneiss are fine-grained hypidiomorphic equigranular with faint foliation evident only in thin section. Quartz, microcline, and plagioclase constitute approximately 90–95% of the leucocratic member and 70–80% of the melanocratic member. Differences in the proportion of biotite and minor hornblende cause the color difference between the two members. Five thin sections for the leucocratic member and three thin sections for the melanocratic member were point-counted (500 points each). For XRD, twelve samples of the leucocratic member and five samples of the melanocratic member from various localities were ground and analyzed. Comparison between point-counting and XRD is shown in Table 4.

Some general observations about this comparison between point counting and X-ray analysis of these rocks can be made. G-1 is considered a homogeneous granite, and therefore the higher standard deviations by XRD technique reflect the error introduced owing to sample preparation and X-ray procedures. The remaining granitoids are *not* homogeneous, and there exists considerable variation in mineralogy for samples collected from different localities. This is reflected in the higher standard deviations obtained for both techniques. The greater standard deviation of the XRD technique may be due to sample preparation and X-ray procedures. As mentioned earlier, the standard deviations can be reduced by longer counting times and more rigorous sample preparation.

CONCLUSIONS

Modal analysis of granitoids by quantitative XRD is a viable technique. The procedure, once calibrated to suit one's needs, is appropriate for performing rapid modal analyses routinely with several advantages over the point-counting method: (1) it is relatively inexpensive and fast, (2) since a powdered bulk sample is used for analysis, obtaining a representative sample is relatively easy, particularly for coarse-grained samples, (3) the method can easily be used for very fine grained rocks, and (4) errors introduced owing to mineral misidentification are minimized. Analyses on actual granitoids have shown favor-

able results. Further potential of this method is discussed in Pawloski (1985). There are limitations to this method that one should be aware of: (1) detection limit is around 2–3% by volume, and the accessory and trace minerals are not identified or quantified, (2) the method requires very careful sample preparation, (3) effects due to compositional and structural variations must be carefully evaluated before application to other rock types. These effects have been taken into consideration for the granitoids. The reader should be cautioned that the procedure as represented here always identifies microcline as a part of perthite. This is the common occurrence for granitoids. If microcline occurs as a separate mineral, this procedure would require modification.

Although the procedure was developed for quartz-feldspar minerals, it can very easily be extended to other minerals by simply calculating appropriate *K* ratio constants.

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