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MODAL ANALYSIS OF GRANITIC ROCKS BY X-RAY DIFFRACTION

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ABSTRACT

A relatively rapid and practical method for determining mineral proportions in granitic rocks by X-ray diffraction is derived from 32 samples of the Cornelia (Arizona) pluton. Forty-three additional samples from that pluton provide an independent test of the method and 41 specimens from the Rocky Hill (California) and Cornucopia (Oregon) plutons test its applicability to other granitoid rocks. Optically derived modes of known precision are used as standards and for testing performance of the method. Quartz, K-feldspar, amphibole and biotite are determined with average errors estimated to be no larger than those associated with optical modes. Average errors for plagioclase probably are somewhat larger in the X-ray estimates. Except for biotite, the X-ray peaks employed seem not to have been used previously in quantitative work of this type, and the data transformations that are integral to the method are new. Estimates derive from fixed-time counts on single peaks for each phase except plagioclase; for it, an intensity-ratio method using all five peaks is employed. A complete analysis for the five phases requires 50 minutes of machine time, with the attention of an instrument technician. Sample powders are prepared and pressure-mounted exactly as for X-ray-fluorescence analysis; thus, the six-minute preparation time per sample (by batch methods) will not constitute an additional cost in many studies. Development work is required for use in other laboratories, but thorough testing shows that the principal capabilities needed by petrologists in the routine study of granitic rock compositions are approximately as well achieved by this method as they are by the microscope.

Keywords: quantitative X-ray diffraction, powder method, X rays, modal analysis, quantitative mineralogical analysis, granitic rocks, intensity-ratio method.

SOMMAIRE

Nous proposons une méthode relativement rapide et pratique d'évaluation par diffraction X de la proportion des minéraux dans les roches granitiques. La méthode a été établie à partir de données sur 32 échantillons prélevés du pluton de Cornelia, en Arizona. Quarante-trois échantillons de ce massif servent de contrôles, et 41 échantillons des plutons de Rocky Hill (Californie) et Cornucopia (Oregon) servent à évaluer l'applicabilité de la méthode à des roches granitiques d'autres complexes. Les résultats d'analyses modales, dont la précision est connue, sont utilisés comme étalons et comme exemples pratiques. La proportion de quartz, feldspath potassique, amphibole et biotite est évaluée avec une marge d'erreur jugée du même ordre de grandeur qu'avec une analyse modale visuelle. Pour le plagioclase, l'erreur moyenne dépasse probablement celle qui serait associée à une analyse modale. Sauf pour la biotite, les pics de diffraction préférés ne semblent pas avoir été utilisés auparavant dans des études quantitatives de ce genre, et les transformations des données qui font partie intégrale de cette méthode sont nouvelles. Le comptage de pics spécifiques pour un temps limité est à l'origine des données de base pour chaque phase sauf pour le plagioclase. Pour cette dernière, c'est une méthode de rapports d'intensité de cinq pics qui est utilisée. Un prélèvement complet des intensités pour les cinq phases requiert 50 minutes de comptage, en présence d'un technicien. Les échantillons doivent d'abord être réduits en poudre et comprimés de la même façon que pour une pastille destinée à une analyse par fluorescence X. Ainsi, la durée de préparation des échantillons en groupe (six minutes chacun) n'occasionnera pas de dépenses additionnelles dans la plupart des études. Un travail de développement sera nécessaire dans les autres laboratoires. À la suite de nos tests détaillés, nous préconisons que pour la plupart des applications ordinaires dans les études pétrologiques des roches granitiques, notre méthode produira des résultats aussi bons qu'avec le microscope.

(Traduit par la Rédaction)

Mots-clés: diffraction X, méthode des poudres, analyse modale quantitative, roches granitiques, méthode des rapports d'intensité.

INTRODUCTION

As petrologists intent on characterizing granitic rocks, we conducted this study to find an alternative to point counting by microscope in establishing the proportions of major mineral phases present (the mode). The standard microscopic method is both tedious and expensive, and a significant sampling problem is posed by medium- to coarse-grained granites. Large thin sections or sawed slab areas must be counted in order to control the precision and accuracy of modes for one hand sample, and several such samples may be required to obtain a representative

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*Deceased.

mode for a single outcrop (Emerson 1964, Morton *et al.* 1969, Chayes 1956). Analysis of large numbers of outcrops readily becomes too expensive to contemplate. This problem can be resolved by making a homogeneous composite of powder bulked from several hand samples if a suitable instrumental method of modal analysis using powders is available. Although not the main concern leading to this study, the power to resolve alteration products by quantitative X-ray-diffraction (XRD) methods also recommends their development for granitic rocks.

The potential of quantitative XRD has been investigated repeatedly since the 1960s, following the important treatise of Klug & Alexander (1954) and Tatlock's pioneering study applied to rhyolites (1966). The current investigation focuses attention on the limited compositional range of granitoid rocks. The method cannot be expected to be more broadly applicable. The narrow scope probably contributes to the finding of a log-linear response of XRD intensities to phase concentration, and permits adoption of a rapid and familiar sample-preparation process that takes no special cognizance of the effects of grinding differences among samples. Furthermore, focusing on granites permits point-count modes to be used as standards in developing calibration curves. Though optical modes are measured with significant error, use of Identity Change numbers (IC numbers, measures of coarseness: Chayes 1956) allows estimation of that error. This study adopts the premise that optical modes of known precision, where available, are preferable as standards both to norms calculated from chemical composition and to preparation of artificial mixtures from pure mineral specimens.

Among the methods previously proposed are a number that might produce useful XRD modes of granites. All, however, have one or two attributes that we were reluctant to adopt. Some require lengthy steps in sample conditioning, or installation of unfamiliar methods and equipment for sample preparation. None have undergone extensive empirical tests of performance on granites. For natural granites, eight samples is the largest number known to the writers to have been used in a sample-by-sample comparison of an XRD method with an alternative. Maniar & Cooke (1987) use 42 samples to compare pluton mean values derived by the two methods, but could not contrast performance on each sample because XRD and optical data originated from different samples and localities. Because we believed that a comprehensive test over a wide range of granitic compositions and fabrics should be required of any method before application, we decided to try to develop a method that had the attributes we desired for routine petrological application. These were: (1) execution speeds appropriate for analyzing hundreds of specimens, (2) use of powders prepared routinely as for X-ray-fluorescence analysis, and (3) performance documented by empirical tests over a broad range of granitic rocks. The method described has the simplicity and speed in routine analysis that we set out to achieve. It was presented in preliminary form as an abstract (Wadsworth & Baird 1985), as was an application to a traverse across the Southern California batholith (Baird & Wadsworth 1985).

To the extent that the design of our study differs from that of most other recent ones, explanation resides in adoption of an empirical, in places statistical, approach. This derives from our inclinations and abilities, rather than from a belief that this approach inherently is superior to another. The differences in philosophy underlying stochastic and deterministic research designs have long been recognized and debated (Leopold & Langbein 1963, Makin 1963). Both types of designs, however, finally will be judged by geologists from their performance in large-scale tests on real specimens of scientific interest. This paper provides such tests for the method proposed.

METHODS

The method was developed using 32 samples from the Cornelia pluton of Arizona (Wadsworth 1968, 1975) as a pilot study. An independent test of the procedure was provided by 43 additional Cornelia samples. To test applicability to other granitic plutons, 31 samples from the Rocky Hill stock of California (Putnam & Alfors 1969) and 10 from the Cornucopia tonalite of Oregon (Taubeneck 1967) were employed. These plutons were chosen because the precision of their optically determined modes is known through Identity Change numbers (Chayes 1956) available for each sample. As a result, the relative amounts of error in XRD and optical methods can be compared. Figure 1 demonstrates the broad compositional range exhibited by Cornelia specimens, and the distinctly different modal compositions of the other plutons. Among the three suites, a large part of the granitic range is encompassed.

Sample preparation

Powder is prepared exactly as it is for X-ray fluorescence (XRF) analysis in our laboratory, using a five-minute grind of plate-pulverized material in a Pica ball mill with a tool steel vial and three steel balls. Particle diameters are expected to range from 0.002 mm to 0.01 mm (Baird & Henke 1965, Madlem 1966). Powders are pressed, without heating, at 700 kg/cm^2 into briquettes 2.5 cm in diameter with 0.2 cm rims and a thick (0.5 cm) backing of phenolic (Buehler, Ltd., No. 20-3500-080). Powdered sample thickness is not controlled other than to be obviously greater than "infinite thickness" to copper radiation.

This thickness requires approximately 1.0 g of granitic rock powder. Pressing dies are similar to those described by Baird (1961) except of smaller diameter. A sample holder was machined from aluminum stock to hold these cylindrical samples under the spring clip of the theta axis of a Philips diffractometer. One benefit that results from adoption of this procedure is that XRD modal analyses and XRF chemical analyses (on unfused powders) can be performed on exactly the same powder surface.

Prior studies have employed lengthy or complex grinding and mounting steps (Otálora & Hess 1969, Petruk 1964, Smith *et al.* 1969), including density separation and analysis of the fractions (Erdosh 1967). A simpler but less familiar preparation involves deposition on a filter from aerosol suspension (Davis & Johnson 1982, Davis & Walawender 1982). Others have added a heavy absorber (Flintner 1975), an internal standard (Bristol 1968), or have blended pairs of samples (Moore 1968). Flintner (1975) pressure-packed his powder, but most others have attempted to achieve random orientation of crystallites. Loading under controlled pressure seems to yield acceptably reproducible packing characteristics, and it has an advantage in simplifying the diffraction spectrum of a complex mixture (by enhancing intensities of some cleavage-favored orientations and reducing others). Samples mounted this way are durable and with moderate care can be retained for many years, a property of particular value for calibration standards.

Instrumentation and operation

Peak searches, and counts made on peaks located, are conducted under software control. The search range selected, the stepping interval within that range, and the fixed-time duration for counting on the peak (Table 1), are selected by the operator. The diffractometer can be programmed to perform successive searches and counts automatically. Search ranges were refined throughout the study as new suites of samples indicated a need for change. The stepping interval was chosen as 0.02° 2θ, with each step counted for 10 or 20 s as a compromise between accuracy of peak location and length of analytical time. To provide day-to-day calibration, the output of the X-ray generator was adjusted to a standard count on the biotite peak of a sample known to exhibit small repositioning errors. The stability of the X-ray generator (powered from a line-voltage regulator) over eight-hour periods was measured as many times better than sample-positioning errors.

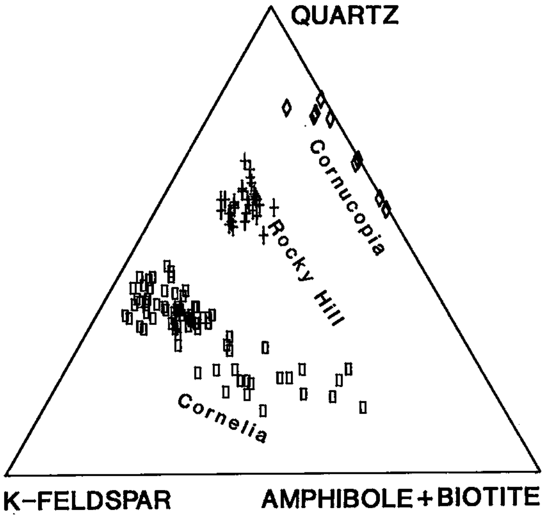


FIG. 1. Variation among all data from the three plutons as defined by optical modes.

Choice of standards

Our decision to use optically determined modes of granitic rocks as standards is based on the wish to be certain that results can be applied appropriately to natural granitic suites. Pure minerals used to fabricate standards cannot be expected to grind identically to rocks. Also, the matrix for major phases in some granites is more complex than artificial mixtures reported in the literature may reflect. Whereas these may not be serious problems in modeling granites, we prefer to avoid the uncertainty. Norms calculated from chemical analyses have been used to define calibration curves in several previous studies. For extremely fine-grained or altered rocks there may be little choice (Tatlock 1966). Flintner (1975) made a strong case that norms are preferable to optical modes because the latter sample too small a volume of rock. The serious deficiency that may exist in this approach, however, is demonstrated by Morton *et al.* (1969), who found exceptionally small chemical variation and extreme modal variation to characterize the same granitoid pluton.

TABLE 1. INSTRUMENT PARAMETERS FOR XRD ANALYSES: PHILIPS ELECTRONIC INSTRUMENTS APD 3520

Mineral	Nominal Peak (°2θ)	hkl	Search Range (°2θ)	Search Steps	Count at Search Step (s)	Peak Count (s)
Biotite	8.82	001	.28	14	20	30
K-feldspar	22.58	111	.28	14	20	60
Plagioclase	31.43	131	.20	10	20	60
Amphibole	33.00	151	.24	12	20	60
Quartz	68.31	301	.20	10	10	30

NOTES: CuKα, 35kV, 20mA, PHA used, graphite monochrometer, no sample spinner; generator output adjusted to standard sample (see text for discussion).

Chung's methods (1974a,b, 1975), which use ratios among reference intensities from random orientation, are simple in concept. They depend, in part, on achievement of random orientation in the sample. The aerosol suspension procedure (Davis & Johnson 1982, Davis & Walawender 1982) has been proposed to accomplish this. We wished, however, to work with sample material prepared identically for both XRD and XRF analyses, and thus to grind and pack samples in the conventional way. The reference-intensity-ratio method also requires appropriate reference standards for the phases involved in an application. There is some uncertainty about the sensitivity of the method to compositional differences in solid-solution phases between the reference standards and the sample unknowns (*cf.* Pawloski 1985, Davis 1987).

A different approach does away with standards and calibration curves in the conventional sense. Zevin (1977) and Starks *et al.* (1984) used major-element chemical data and XRD intensities in multivariate statistical designs to derive XRD modes. This approach does not meet our need for a rapid and simple procedure. Rocks of the Cornelia pluton could require both XRD and chemical analyses of nine or more subsamples for each sample whose XRD mode we sought to determine.

Peak selection

Ninety-two peaks in the range from 4° to 75° 2*θ* were identified among chart scans for 25 Cornelia specimens, and correlation was inspected between peak height and phase concentration known from optical modes. Seventeen peaks that seemed to have potential were remeasured by fixed counts made on peak maxima. Selection among alternate peaks for a given phase was based on the degree of scatter observed about the regression curve of X-ray intensity on concentration. Decisions were simply made because the peaks selected performed distinctly better than their alternatives. The 110 and 151 hornblende peaks provide an example. As the principal hornblende peak, and the only principal peak of any phase clearly free of interference, 110 was the most obvious candidate for quantitative use among all 92 peaks. Linear calibration-curve fit to 25 samples was 65%, increasing to 66% and 75% as first one, and then three, extreme values were deleted. Corresponding fits for calibration using the much smaller and less isolated 151 peak were 74%, 86% and 91%. The two cases were reasonably comparable because both data sets had precisely three distinct (though different) outliers. This difference in performance is significant and reproducible, so the 151 peak (Fig, 2) was selected for amphibole determinations. The source of greater dispersion in intensities from 110 is not known, but it could relate to variation in degree of preferred orientation for these cleavage planes. Most of the extreme outliers in intensities from 151 are caused by interference from hematite or orthopyroxene (or both). Among 85 samples for

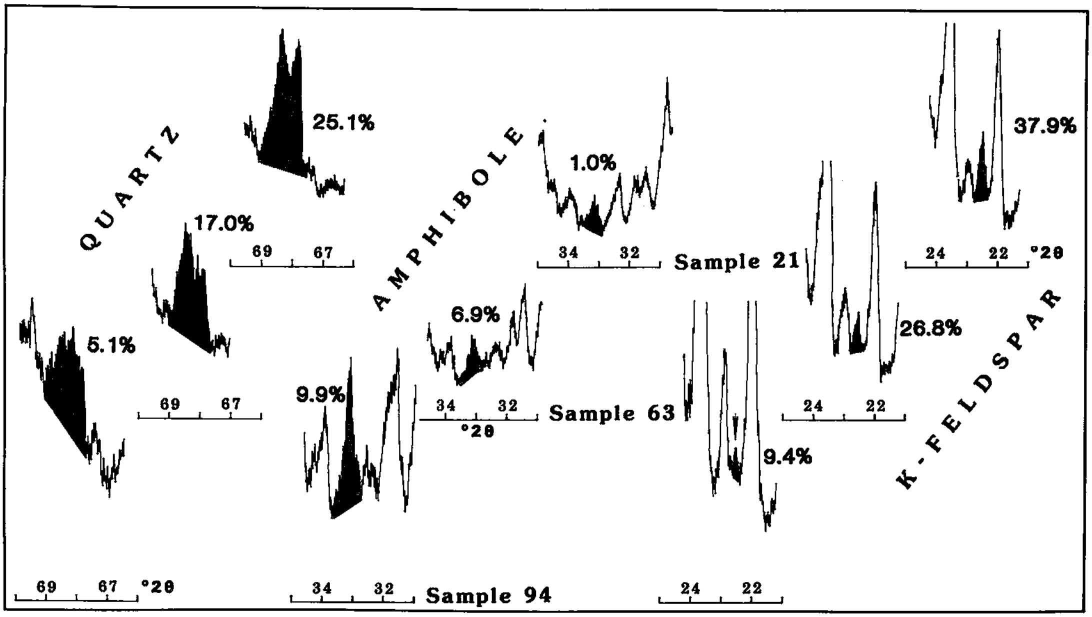


FIG. 2. Tracings of the diffraction spectra surrounding peaks measured for three minerals, in three samples of the Cornelia pluton. Percentages are optically determined modal contents. Chart recorder full-scale setting for scan of sample 94 was half that of the other two samples. Scans made during peak selection, using an older-model Philips diffractometer that was replaced prior to quantitative work.

which hornblende was determined in this work, four Cornelia specimens yielded anomalously high intensities for 151. These samples were unique in containing an obvious rim of hematite on magnetite, as well as significant orthopyroxene. Orthopyroxene-bearing samples without visible hematite yield reasonable hornblende estimates in this study.

The principal biotite peak 001 is the best available choice for this phase despite interference from muscovite. Many granitoid rocks, including the three plutons employed here, contain only minor muscovite. For two-mica granites, it would be necessary to develop calibration curves for ratios between the micas. The only K-feldspar peak that performs satisfactorily, 111, is very small (Fig. 2), and has not been employed for quantitative work previously. Orthoclase is the species present in plutons of this study, but an early application of the method in our laboratory (Cornell 1985) suggests that microcline concentration can be estimated satisfactorily from the same peak and calibration function by applying a shift in peak-search range to 22.22–22.50° 2θ. The quartz "peak" selected here probably has been avoided in previous work of this type because several quartz reflections combine over a broad 2θ range, and the overall pattern is complex (Fig. 2). Nevertheless, the search range cited in Table 1 works very well, and its center is unchanged from the first selection made for it in initial work. The 301 reflection probably is most often selected by the search parameters of our method. We investigated many plagioclase peaks, none of which performed well. The moderate-intensity 131 peak produced the best-fitting and most linear calibration curve.

Data treatment

In defining calibration curves, observed count-rates are converted to logarithms before averaging multiple readings and fitting linear functions of XRD log-intensity *versus* concentration. We choose to transform the data, rather than adopting the more usual procedure of fitting the observations to a theoretically appropriate curve, for two principal reasons. The first is that we do not know how to determine the appropriate function from X-ray theory. The procedures followed depart in too many ways from those which clearly permit acceptance of an established relationship between intensity and concentration. For example, mass-absorption coefficients are not considered, background intensity is not determined, and phases will adopt differing degrees of preferred orientation in response to packing under pressure. An exponential relationship probably should be expected, but the specific type is unclear. The second reason is statistical in nature, with transformation required in order that tests on the data can employ the most efficient and powerful statistics: those which require data to have a normal (Gaussian) distribution.

Both concentration and intensity variates are involved. Compositional variables for major components (quartz and the feldspars) have positive binomial distributions that provide a sufficient approach to normality without transformation. Compositional variates with relatively low abundance and a tendency to cluster (*e.g.*, amphibole and biotite in this study) in some cases can be shown to follow the negative binomial distribution (Griffiths 1967, p. 297). The arcsine transform is used to produce a normal distribution in these cases, and we do employ it on amphibole in fitting the calibration function. Specifically, we use: arcsin [(amphibole proportion + 0.005) $^{0.5}$]. Whereas regression fit for amphibole improved after transformation, resulting in slightly better estimates, the fit was unaffected for biotite, and no transform is used for it. Observed data tend to describe exponential trajectories in scatter diagrams of intensity *versus* concentration (Fig. 3B). In addition, this figure displays increased dispersion at higher concentrations, implying that a proportional relationship exists between mean and variance in the intensity data. A logarithmic transform is indicated in order to produce a more nearly normal distribution, with mean and variance uncorrelated (Griffiths 1967, Table 15.1).

These are some of the observations and reasoning that led to use of transformations. Evidence that they are appropriate for the intended purposes is provided by the linearity of the calibration functions after transformation, and the production of more equal dispersion throughout their extent. One small test of an alternative procedure was conducted using data plotted in Figures 3A and 3B. The general second-order polynomial (parabolic) function was fitted to data in the latter. In comparison to an 80% fit of the linear function to these untransformed data, the curvilinear fit is 83%. As indicated in Figure 3A, the log-linear fit is 89%. Quartz content was estimated for 43 independent Cornelia samples from both the log-linear and parabolic functions. Estimates from the latter curve showed slightly larger average errors (–1.3 modal % bias, *versus* –1.0%; 2.3% average residual, *versus* 2.0%; and 12% error relative to the amount present, *versus* 10%). These differences are fairly small and might disappear with choice of some other exponential function of better fit. A much more important aspect is exemplified by the comparison (in later discussion of Fig. 3D) of optical and XRD errors. The conclusion reached there, that quartz concentration (on average) is determined at least as well by XRD modes as by optical modes, could only be made with reasonable confidence and clarity because the data involved have normal distributions, and their standard deviations, therefore, have known expectations.

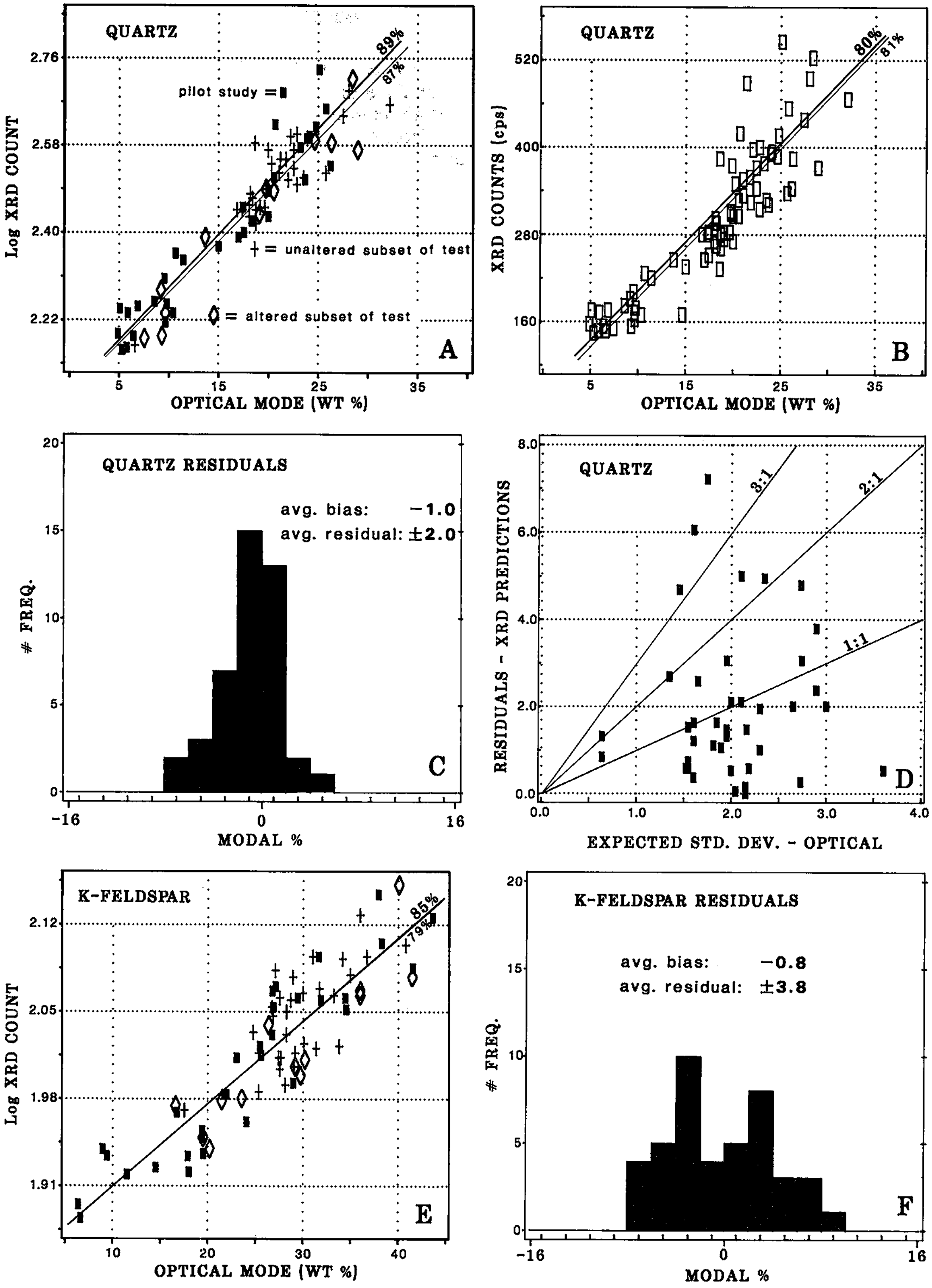


FIG. 3. Cornelia pluton pilot study (n = 32) and test (n = 43) results for quartz and K-feldspar. A,B,E: heavier regres-

A ratio of X-ray count rates of pairs of peaks has been suggested to reduce differences produced among samples by differential response to some common treatment (*e.g.*, grinding). Intensity ratios also have been proposed as means to reduce the impact of matrix-absorption differences among samples (Otálora & Hess 1969) or minor changes in machine factors such as alignment and tube output with aging (Goehner 1982). All possible binary ratios among the five phases were investigated. Intensity ratios with the quartz peak displayed the strongest correlations with the corresponding concentration ratios. Thus we could adopt a form of Pawloski's procedure (1985) to compute compositions, in which the quartz peak serves as the denominator common to ratios formed with the other four phases. The estimated mode may be computed by simultaneous solution of five equations, four with the form $I_{\text{min}}/I_{\text{quartz}} = a + b(X_{\text{min}}/X_{\text{quartz}})$. The fifth expresses the expected concentration sum of the five minerals: $(X_{\text{min 1}} + \ldots + X_{\text{min 5}}) = 97$. For future applications, 97% (the approximate optical-mode average sum among all the samples of this study) normally will be used as the expected sum, though the observed optical sum was employed for the calibration and tests reported here. Much better performance resulted from compound ratios, however, in the form $I_{\text{min}}/(I_{\text{min}} + I_{\text{quartz}})$, substituting this ratio and its concentration equivalent for the simple ratios in linear equations corresponding to the one above. Otálora & Hess (1969) used ratios in this form. The significance of compound ratios in our work is that they provide considerably better plagioclase estimates than are obtainable from the plagioclase peak used alone.

PILOT STUDY

Analysis of variance

In repeated measurement of an X-ray count rate on a peak for splits of one sample, variability originates in grinding, splitting, packing, positioning the sample in the beam, finding the peak and accumulating counts on it. In order to discriminate among samples of significantly different modal composition, it might be necessary to lower variability by replication at any one (or several) of these procedural steps. Analysis of variance (ANOVA) provides the means to decide if replication is necessary. For this purpose, three rock samples were selected randomly from each of three large granitic suites readily available at the inception of our study: the Cornelia pluton, the Lakeview Mountains pluton of southern California (Morton *et al.* 1969), and a traverse across the Southern California batholith (Baird *et al.* 1979).

Preliminary work had indicated relatively low variance for biotite in response to sample position in the diffractometer, and quartz seemed to show the largest. The expectation was that biotite would vary most among replicate pressings of a single sample because of orientation effects, and that quartz would be the least affected. Therefore, these two minerals were included in the ANOVA design summarized in Table 2 (replicate counting without repositioning of the sample was known to yield sufficiently low error that a separate level of nesting was not required for it). We were interested in discriminating samples within individual plutons rather than among plutons, so the results were interpreted to imply no need for replication, either of pressings or of counts on repositioned samples. During repeated counts on the 32 pilot-study specimens, however, quartz variability by position was found to exceed these ANOVA results substantially, and two replicates for it were added to the procedure.

The ANOVA design adopted for the other three peaks (Table 3) deletes replicate pressings based on the outcome described above. Because three samples inadequately represent within-pluton variability, the conservative approach seemed to be a non-nested series of ANOVAs among which results for the worst

TABLE 2. MODEL II, NESTED ANALYSIS OF VARIANCE; QUARTZ AND BIOTITE XRD PEAKS

Source of Variance	Quartz				Biotite			
	df	SS	MS	F	df	SS	MS	F
Among plutons	2	.2730	.1365	1.66[a]	2	4.1581	2.079	4.61[b]
Among samples within plutons	6	.4941	.0823	9.75[b]	6	2.7036	.451	70.83[b]
Among pressings within samples	18	.1521	.0084	.89[a]	18	.1145	.006	9.29[b]
Among positions within pressings	54	.5010	.0093		54	.0370	.001	
Total	80	1.4201			80	7.0132		

NOTES: Original data are logarithms of XRD peak intensities; F = Fisher ratio; MS = mean squares; SS = sums of squares; df = degrees of freedom. [a]not significant at .05. [b]significant at .01.

sion line for pilot study, lighter one for all 75 samples; percentages on regression lines = 100 r^2 (count data are untransformed in B). C,F: residuals from XRD estimates for 43 test samples using pilot-study regression functions. D: comparison of precision of optical and XRD modes (see text for discussion).

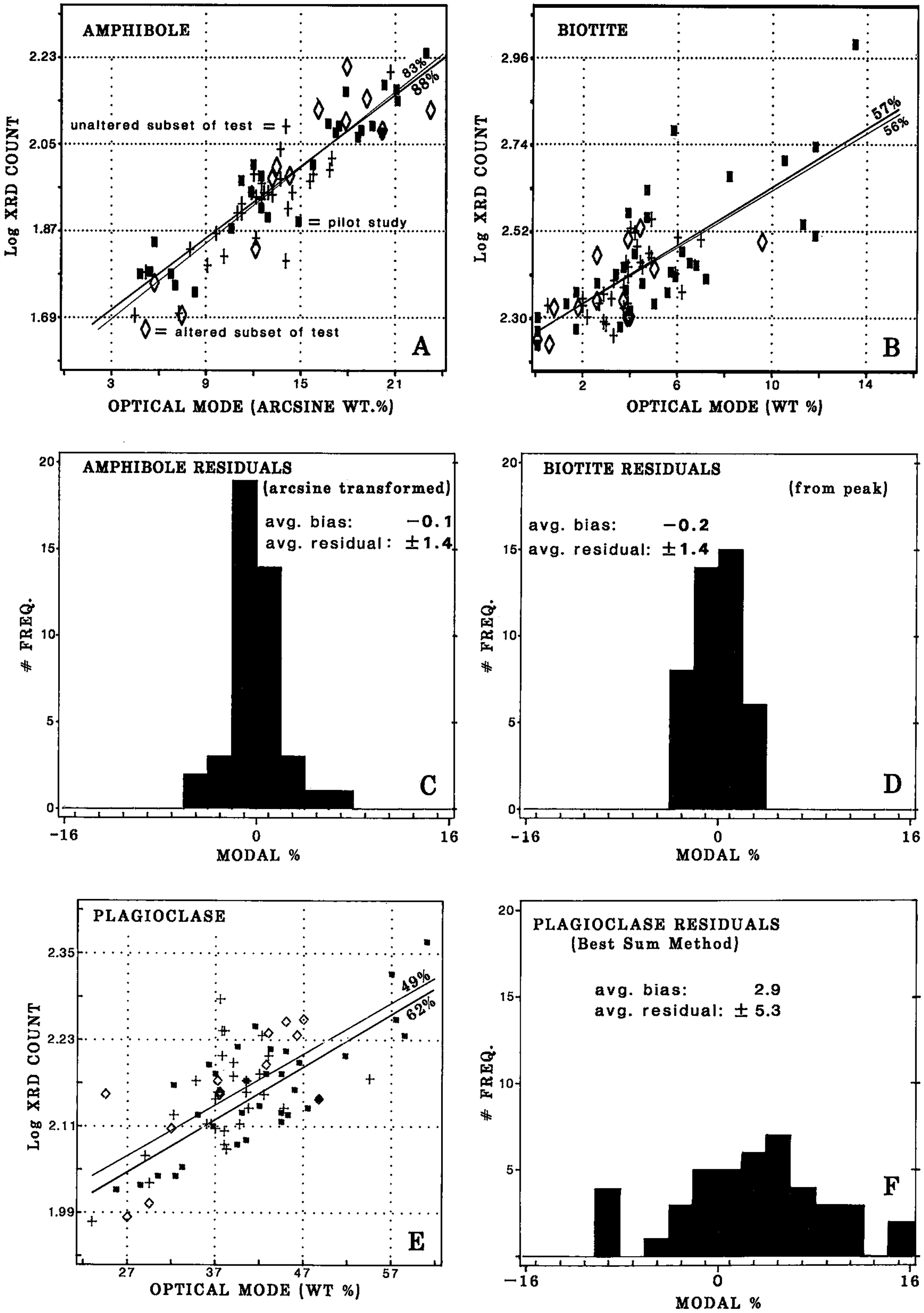

AMPHIBOLE
Log XRD COUNT
2.23
2.05
1.87
1.69
unaltered subset of test = +
■ = pilot study
◊ = altered subset of test
83%
88%
A
3
9
15
21
OPTICAL MODE (ARCSINE WT.%)
BIOTITE
2.96
2.74
2.52
2.30
57%
56%
B
2
6
10
14
OPTICAL MODE (WT %)
AMPHIBOLE RESIDUALS
(arcsine transformed)
avg. bias: −0.1
avg. residual: ±1.4
FREQ.
20
15
10
5
0
C
−16
0
16
MODAL %
BIOTITE RESIDUALS
(from peak)
avg. bias: −0.2
avg. residual: ±1.4
D
PLAGIOCLASE
2.35
2.23
2.11
1.99
49%
62%
E
27
37
47
57
OPTICAL MODE (WT %)
PLAGIOCLASE RESIDUALS
(Best Sum Method)
avg. bias: 2.9
avg. residual: ± 5.3
F
MODAL %

TABLE 3. MODEL II, ANALYSES OF VARIANCE; K-FELDSPAR, AMPHIBOLE AND PLAGIOCLASE XRD PEAKS

Source of Variance		Cornelia Pluton			Lakeview Mtns. Pluton			So. Cal. Batholith		
		df	MS	F	df	MS	F	df	MS	F
K-Feldspar:	Among Samples	2	.0148	4.09[a,d]	2	.0007	7.46[b]	2	.0416	42.3[b]
	Among Positions	10	.0036		12	.0001		12	.0010	
	Total	12			14			14		
Amphibole:	Among samples	2	.0941	17.4[b]	2	.0131	2.38[a,d]	2	.1115	306.8[b]
	Among positions	10	.0054		12	.0055		12	.0004	
	Total	12			14			14		
Plagioclase:	Among samples	2	.0159	3.02[a]	2	.0371	5.64[c]	2	.0389	2.58[a,d]
	Among positions	10	.0052		12	.0065		12	.0151	
	Total	12			14			14		

NOTES: Original data are logarithms of XRD peak intensities; df = degrees of freedom; MS = mean squares; F = Fisher ratio. [a]not significant at .05. [b]significant at .01. [c]significant at .05. [d]recommendations based on this as worst case for this phase among the three plutons.

performing of the three plutons for a given mineral would be used to guide recommendations. Those cases are labeled in Table 3. It was concluded that counts on K-feldspar had to be replicated in a second position, and amphibole and plagioclase in three positions.

Positioning of the sample in the X-ray beam yields the largest variance of concern to the proposed method. A few samples that produced widely divergent counts upon repositioning were found to behave within expected bounds after production of a new briquette. We infer that eccentric shape of a briquette can cause extreme variability due to its effect on sample position in the X-ray beam. A sample spinner was not available for this study, but it is probable that less sensitivity to position would result from its use.

Calibration curves

The relationships of XRD count rates to optically derived modal data are not plotted separately for the pilot study, but pilot-study samples can be discriminated by symbol in Figures 3 and 4 among all 75 Cornelia samples. Percent r^2 values (coefficients of determination) in these figures and Table 4 express the degree of fit of the estimated linear-regression functions for the 32-sample pilot study and larger sets of samples. For use in estimation of unknowns, one hopes to have values near or exceeding 90%, a value closely approached for K-feldspar, quartz and amphibole. Poorer fits for biotite and plagioclase are much improved if those peaks are used to form compound ratios with the quartz peak (Table 4).

Sources of error

The dispersion of points in the scatter diagrams of Figures 3 and 4 arises from several factors other

TABLE 4. LINEAR REGRESSION SUMMARY

Optical Variate (x)	Regression Parameters				
	Data Set[a]	n	Intercept	Slope	Fit (r^2)
QUARTZ	1	32	2.07	.0219	.89
	2	75	2.07	.0212	.87
	3	116	2.13	.0173	.83
K-FELDSPAR	1	32	1.84	.0067	.85
	2	75	1.84	.0066	.79
	3	116	1.83	.0069	.89
AMPHIBOLE[b]	1[c]	27	1.63	.0248	.88
	2[c]	70	1.60	.0266	.83
	3[c,d]	80	1.58	.0276	.84
BIOTITE	1	32	2.26	.0368	.57
	2	75	2.26	.0360	.56
	3	116	2.26	.0414	.64
PLAGIOCLASE	1	32	1.85	.0073	.62
	2	75	1.88	.0070	.49
	3	116	1.87	.0069	.54
KSPAR/(KSPAR + QUARTZ) . . .	1	32	39.73	.0937	.28
	2	75	37.46	.1288	.43
	3[e]	116	40.10	.0836	.80
AMPH./(AMPH. + QUARTZ)[b] . .	1[c]	27	37.28	.1633	.90
	2[c]	70	36.86	.1743	.90
	3[c,d]	80	36.63	.1777	.90
BIOTITE/(BIOTITE + QUARTZ) .	1	32	47.13	.1207	.74
	2	75	47.02	.1276	.70
	3	116	47.07	.1254	.67
PLAG./(PLAG. + QUARTZ) . . .	1	32	34.19	.1801	.86
	2	75	34.88	.1738	.84
	3	116	34.51	.1768	.82

NOTE: All ratios are expressed as percentages.

[a] 1 = pilot study; 2 = all Cornelia pluton; 3 = all plutons.

[b] Arcsine-transformed amphibole values are used.

[c] Excludes five extreme values (probable hematite and/or hypersthene interference in four of them).

[d] Not determined for Rocky Hill stock; less than 4% observed.

[e] Curvilinear fit would improve this; not performed.

FIG. 4. Cornelia pluton pilot study ($n = 32$) and test ($n = 43$) results for amphibole, biotite and plagioclase. A,B,E: heavier regression line for pilot study, lighter one for all 75 samples; percentages on regression lines = 100 r^2: C,D,F: residuals from XRD estimates for 43 test samples using pilot-study regression functions (see text for derivation of best-sum estimation procedure, which results in F).

than error in the XRD procedure. For example, the XRD data are derived from a much larger volume of rock (a hand sample) than are the optical modes (a thin section from the same hand sample), so the two methods estimate properties of samples that differ to an unknown degree. A significant amount of the scatter observed in all relationships is due to imprecision in the optical modes. All represent point counts from a single thin section, employing areas between 590 and 620 mm^2 and total counts ranging from 1600 to 2100. IC numbers based on 25 mm traverse lengths range from 30 to 165, with a statistical mode near 65. From the charts of Chayes (1956), standard deviations for reproducibility should average approximately 2 modal % and range from 0.3 to 3.5% for the major mineral components. Minerals present at 10–15% or less will be determined with a lower (but unknown) precision compared to that known for the major components.

Accuracy of optical modes is dependent on correct identification of phases, but also on operational definitions of the petrographer. Cornelia modes derive from earlier work aimed at understanding magmatic history, in which hydrothermal alteration was ignored wherever possible. Therefore, chlorite produced by alteration of biotite is recorded as biotite in the optical modes, but will not be so recognized in XRD modes. Optical discrimination between feldspar species was a problem of varying degree owing to very fine-grained alteration. A minor source of error in XRD modes is produced in the conversion of optical-mode data to weight percentages, using densities inferred from incomplete information about the composition of the phases. These sources of error in optical modes used as standards have to be recognized when attempting to judge the XRD procedure's capability.

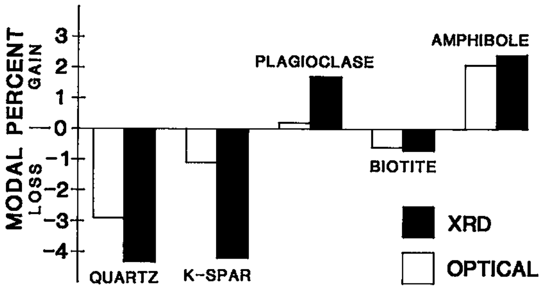


FIG. 5. Gain/loss diagram for average modal % changes produced hydrothermally in the slightly altered subset of the Cornelia pluton test, when compared to the unaltered subset. Results from XRD modes and optical modes are contrasted.

TESTING THE METHOD

Calibration curves are defined by linear regression of log XRD-intensity on optical mode %. The latter variable contains measurement error. If this were not the case, confidence limits could be fitted to the regression function, which would express the error expected in estimation of modal percentages from the function. Because measurement error in optical modes invalidates this formal statistical procedure, error of estimation is determined empirically against other test samples for which optical modes are available. In application, the independent variable (modal %) is predicted inversely from measurement of the dependent variable (log XRD count rate). Williams (1983) would reverse the variates in fitting the regression, claiming that the one to be estimated always should be regressed as the dependent variable. This recommendation is considered to be inappropriate. One reason is that the pilot-study samples were not selected randomly, but were picked to span the compositional range of the pluton. If this procedure introduced what statisticians term "fixed effects" (to be conservative, that has to be assumed), then the variable having those effects should be regressed as the independent variate (*cf.* Wadsworth 1984, Williams 1984, Sokal & Rohlf 1969, Chapt. 14).

The Cornelia pluton test

Forty-three Cornelia samples were available for an independent test. Because all Cornelia specimens may contain the effects of minor alteration, and because these can produce additional error in optical modes, records of the optical study were reviewed; 13 of the 43 samples were marked as of lesser quality owing to identification problems noted. Figure 5 contrasts the mean values for each mineral species in the two subsets, as determined by optical and XRD methods. Most subset differences in mean value, regardless of the method used, can be attributed to hydrothermal alteration. Lesser content of K-feldspar and biotite, and greater plagioclase and amphibole (secondary "actinolite") in the subset of 13 agree with differences known to exist in altered specimens. This result suggests that fairly fine discrimination can be accomplished using means of XRD-mode data. Also, because alteration effects were ignored where possible in the optical modes but not in XRD modes, the larger differences observed between the two sets from XRD estimates may provide evidence of the accuracy inherent in XRD modes.

Test samples generally plot within the bounds of pilot-study data in the scatter diagrams of Figures 3 and 4, and regression functions based on 75 Cornelia samples are very similar to those based on the pilot set of 32 (Table 4). The degree to which the two subsets of test samples fit the regression functions is similar, though altered samples have slightly higher dispersion. The best estimates, overall, are for quartz (Figs. 3A–D). Residuals from 43 determinations are the smallest for this phase relative to the amount present. Figure 3D is especially instructive in weighing the relative capabilities of XRD and optical modes. Observed residuals from XRD-based quartz estimates are plotted against the standard deviations expected for quartz abundance determined by point counting. These standard deviations derive from Chayes (1956, Fig. 10, p. 77), based on a 625 mm^2 area of analysis and IC numbers available for 40 of the 43 test specimens. Theoretically, in a sufficiently large sample, 68% of the observations should lie on or beneath the 1:1 line in Figure 3D if no error is contributed from the XRD estimates (*i.e.*, if the only error is in determining the optical modes). Our data fit this "expectation" precisely. Ninety-five % of all the samples should have residuals plotting on or below the 2:1 line, given the same hypothesis about sources of error, but only 35 of the 40 (87%) do so. Three points represent XRD residuals too large to be accounted for by three standard deviations of optical-mode error. We interpret these results to mean that significant error in the XRD-based quartz estimates can be proved in perhaps only four or five of 40 cases; for the other 35–36, all the error could exist solely in the optically derived standards. There is error in all XRD estimates, of course, but this plot demonstrates that it is at least as small as the optical error in most cases.

Residuals from K-feldspar estimates (Fig. 3F; Table 5) are only slightly larger than quartz residuals if expressed as a percentage of the amount present (termed "relative error" or "percent error", henceforth). Optical modes are likely to be less precise for K-feldspar also, because it typically is coarser grained than quartz, and alteration effects produce some identification errors for it. In addition, the X-ray peak used for K-feldspar is very small (Fig. 2), and the slope of the calibration curve is much flatter than for other phases (this is not evident in Figure 3 because of axis scaling, but compare numerical values for slope in Table 4). Therefore, the calibration curve for K-feldspar is most susceptible to variation arising from small changes in machine factors, such as alignment or X-ray tube aging, which would not produce equally significant effects in the other calibrations.

Relative error for amphibole and biotite (Figs. 4C, D; Table 5) is significantly higher than for the other two phases. Because amphibole and biotite are not major components, their optical-mode precision must be lower as well. XRD modes cannot distinguish and rank samples adequately in the 0–3% range, but optical modes reported here cannot do so either. Dispersion in the biotite scatter diagram (Fig. 4B) is greater than in all others, as is reflected in the poor fit of the regression function. It is interesting that biotite counts did not need replication because they showed less repositioning variance than the other phases, yet we cannot predict biotite as well as the others. Four reasons occur to us: (1) our small test of packing variability was not adequate, and replicate mounts may, in fact, be desirable; (2) biotite is less abundant, on average, than other phases, so that the optical modes are less precise; (3) the common alteration of biotite to chlorite was ignored purposely in optical modes, and thus they are inaccurate by original design; and (4) though there is little visible muscovite in these rocks, variable amounts surely are present in the ubiquitous alteration products of the feldspars. Because the principal biotite and muscovite peaks coincide, some interference effects can be expected.

Estimates for plagioclase that derive from the 131 peak are not satisfactory. The calibration curve fit to pilot-study data is relatively poor (Fig. 4E), and estimates derived from it for the Cornelia test set have significant positive bias and some extreme residuals (maximum of +24 modal %). The analysis of intensity ratios is described in detail here because the ratios provide means to make better estimates of plagioclase. Simple $I_{\text{min}}/I_{\text{quartz}}$ ratios perform very poorly, however (Table 5). Pilot-study calibration functions for these ratios provide poor fit to the data, which are both nonlinear and disperse, and which yield large negative estimates of concentration ratios in 19 of 43 cases. This leads to physically impossible results for two or more phases in those 19 samples when the equations are solved simultaneously. The remaining 24 samples display large estimation errors, as well. Compound ratios yield much better calibration-curve fits and resulting estimates (Tables 4, 5). Given these new estimates from compound ratios for the five phases, comparative data in Table 5 indicate that the best estimates for quartz, K-feldspar, amphibole and biotite in the Cornelia test set derive from single-peak intensities. Because the same intensity data are used for all computational schemes, it can be recognized that solution of simultaneous equations has the effect of distributing the analytical error among the five concentrations determined. The process results in lesser error for the predominant phase (plagioclase) than occurs by estimation from 131 intensity alone, and greater error for each of the other minerals. In compositional estimates for unknowns using ratios, error distribution among the phases will be uncertain. Therefore, Pawloski (1985) emphasized that the maximum error observed among the phases during testing should be cited as a single error expectation for all phases in this form of analysis.

The data permit six partially independent ways to estimate plagioclase: (1) 131 peak intensity, (2) sim-

TABLE 5. ALTERNATIVE METHODS OF XRD-MODE ESTIMATION - SUMMARY STATISTICS FOR THREE TEST PLUTONS

PHASE	SOURCE OF ESTIMATE	REGRESSION FIT	AVERAGE SAMPLE ESTIMATION ERRORS			VARIATION AMONG TEST-SET SAMPLES			
		r^2	Bias[a]	Residual[b]	%Error[c]	Optical $\bar{X}$	Mode s	XRD $\bar{X}$	Estimate s
CORNELIA PLUTON TEST (N = 43)									
Quartz	Single Peak	.89	-1.0	2.0	10	19.8	5.7	18.8	6.1
	Simple Ratios[d]	n/a	-1.0	4.5	26			-----	---
	Compound Ratios	n/a	0.2	2.8	15			20.1	8.0
K-feldspar	Single Peak	.85	-0.8	3.8	13	29.3	5.7	28.5	7.2
	Simple Ratios[d]	.30	-5.8	6.7	24			-----	---
	Compound Ratios	.28	-3.3	5.4	19			26.0	4.9
Amphibole	Single Peak	.88	-0.1	1.4	28	5.0	3.3	4.9	3.9
	Simple Ratios[d]	.71	0.4	2.5	48			-----	---
	Compound Ratios	.85	-0.3	1.6	41			4.8	3.8
Biotite	Single Peak	.57	-0.2	1.4	38	3.7	1.8	3.6	2.3
	Simple Ratios[d]	.63	-0.0	2.1	70			-----	---
	Compound Ratios	.74	-0.4	1.5	95			3.3	2.3
Plagioclase	Single Peak	.62	2.5	6.4	17	38.2	6.2	40.9	3.9
	Simple Ratios[d]	.76	6.5	8.4	22			-----	---
	Compound Ratios	.86	3.5	5.2	15			41.7	5.1
	Ratio w/Quartz	n/a	2.8	6.3	16			41.0	9.6
	Difference Calc.	n/a	1.2	5.9	16			39.4	7.7
	Best Sum	n/a	2.9	5.3	14			41.1	7.9
ROCKY HILL STOCK TEST (N = 31)									
Quartz	Single Peak	---	-4.9	4.9	16	30.9	2.3	26.0	2.5
	Compound Ratios	---	1.4	3.1	10			32.2	2.9
K-feldspar	Single Peak	---	-2.9	3.5	25	13.7	2.0	10.9	2.8
	Compound Ratios	---	-2.8	3.2	22			10.9	1.9
Amphibole[e]	Single Peak	---	----	---	---	2.0	1.0	----	---
	Compound Ratios	---	----	---	---			----	---
Biotite	Single Peak	---	2.0	2.2	31	7.5	1.3	9.5	1.4
	Compound Ratios	---	1.6	2.1	30			9.1	2.2
Plagioclase	Single Peak	---	-7.2	7.3	16	45.4	2.8	38.2	4.9
	Simple Ratios	---	----	---	---			-----	---
	Compound Ratios	---	-0.3	3.0	7			45.0	3.1
	Ratio w/Quartz	---	-8.9	8.9	19			36.4	3.6
	Difference Calc.	---	5.4	5.5	12			50.7	3.6
	Best Sum	---	-0.3	3.0	7			45.0	3.1
CORNUCOPIA TONALITE TEST (N = 10)									
Quartz	Single Peak	---	0.3	2.5	11	24.8	5.3	25.2	4.1
	Compound Ratios	---	-0.6	3.2	12			24.3	6.8
K-feldspar	Single Peak	---	0.4	1.1	356[f]	0.7	1.1	0.9	1.7
	Compound Ratios	---	4.2	4.4	2855[f]			4.9	2.0
Amphibole	Single Peak	---	-0.1	1.2	560[f]	1.8	2.4	1.8	2.0
	Compound Ratios	---	0.0	0.1	61			1.8	2.5
Biotite	Single Peak	---	1.0	1.8	25	7.1	0.8	8.1	2.0
	Compound Ratios	---	-1.6	2.0	29			5.5	2.4
Plagioclase	Single Peak	---	2.8	5.8	9	63.3	2.9	66.1	7.6
	Simple Ratios	---	----	---	---			-----	---
	Compound Ratios	---	-2.1	4.2	7			61.2	4.5
	Ratio w/Quartz	---	2.6	8.9	14			65.9	13.0
	Difference Calc.	---	-0.2	3.4	5			63.1	4.6
	Best Sum	---	-1.5	4.1	7			61.8	4.9

NOTES: All estimates based on calibration curves from Cornelia pluton pilot-study regressions. For ease in simultaneous solution, ratio-data regressions did not use arcsine transform for amphibole.

[a] Bias = (XRD estimate - optical estimate).

[b] Residual = absolute value (XRD estimate - optical estimate).

[c] % error = (residual • 100) / optical estimate.

[d] Deletes 19 of 43 samples which yield physically impossible results.

[e] Not determined by XRD.

[f] Large values result from near absence in optical mode.

ple ratios of all peaks to the quartz peak and simultaneous solution of five equations, (3) the compound form of these ratios and simultaneous solution of equations involving them, (4) solution of only the compound ratio for plagioclase given the single-peak estimate for quartz, (5) a difference calculation using the expected analytical sum and the four single-peak estimates, and (6) a "best-sum" estimate described below. For true unknowns, four of these computations yield plagioclase estimates that can be used to arrive at an analytical sum, given concentrations derived from single-peak intensities for the other four phases. Simple ratios are excluded, leaving (1), (3) and (4), above. The best-sum procedure selects the plagioclase estimate, among the three, that yields the sum closest to that expected. Among Cornelia test-set samples, the estimate for plagioclase judged best on this basis derived almost equally often from each of the three sources. On the other hand, the best sum for every specimen of the Rocky Hill stock occurred when plagioclase was estimated using compound ratios, so the best-sum result is identical to the latter (Table 5). The best-sum and difference computations remain as alternatives for application and can be compared in Table 5. The difference calculation works best for the Cornelia test set, with the "best-sum method" nearly as effective. Tests on the other plutons suggest that the best-sum approach be adopted for general application. The average relative error of plagioclase best-sum estimates (Table 5) is similar in magnitude to the smallest relative errors obtained for the other major components (quartz and K-feldspar), the latter derived from single-peak estimates. Nevertheless, these best estimates for plagioclase are less satisfactory to us than are those we obtain for other phases. The largest residual among the 43 Cornelia test samples (+15 modal %; Fig. 4F) is considerably larger than any we believe likely to occur in point counts of thin sections. In our experience, also, there commonly is less relative variation in plagioclase concentration within plutons than there is for other important phases. Thus, whereas smaller relative error in estimation of plagioclase probably is desirable, this method cannot achieve it.

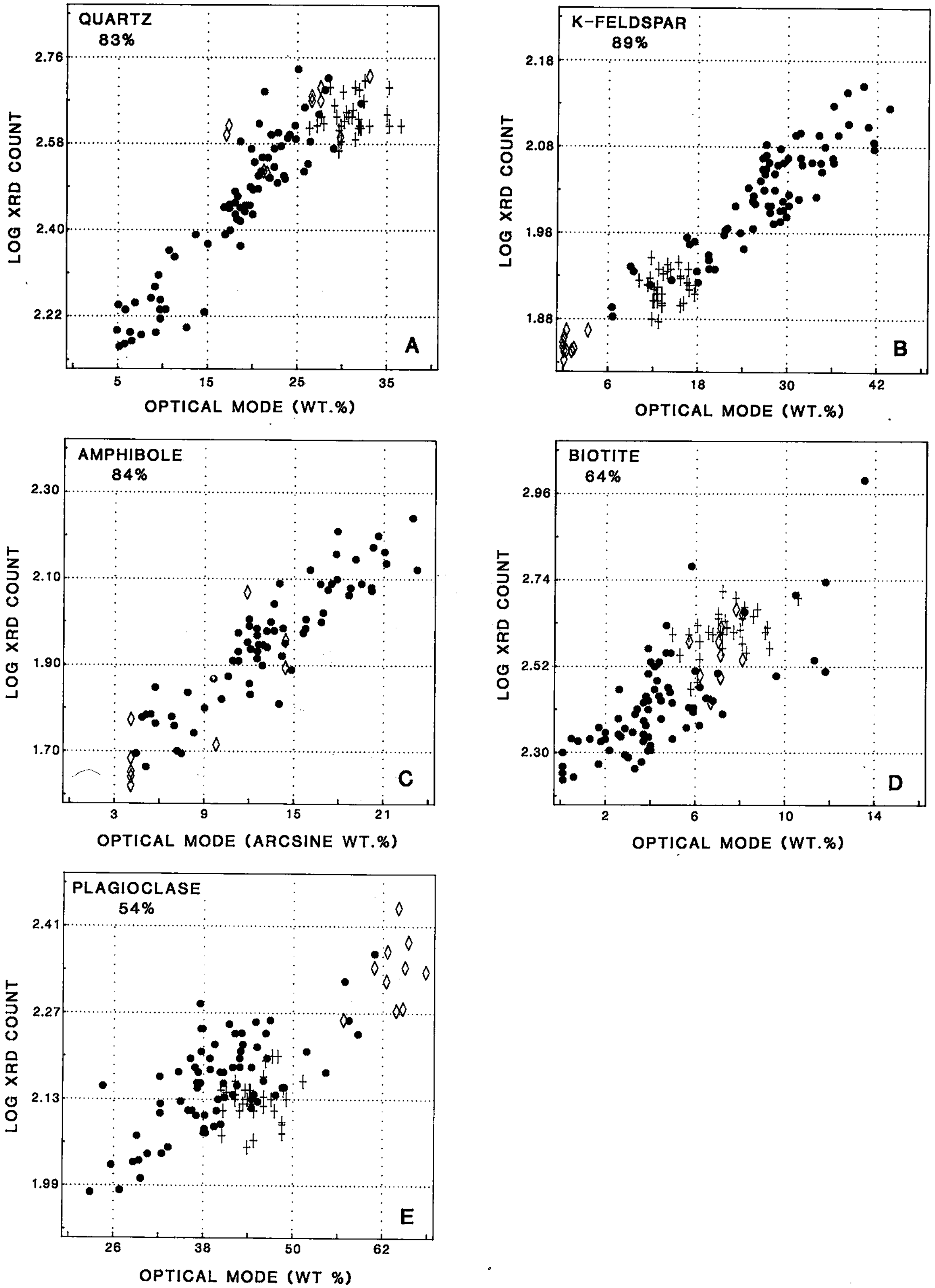
Tests on other plutons

Samples were obtained of the Rocky Hill stock and Cornucopia tonalite because optical modes had been determined for them with great care. Putnam & Alfors (1969) point-counted 4000 mm^2 sawed slabs (both sides in some cases) with a stereomicroscope, overlaying a 1.5 mm grid sheet and counting an average of 2000 points per side. They reported average expected modal error of 2% based on point-count area and coarseness estimated by IC numbers. Thus, precision appears to be approximately comparable to the Cornelia data. In their study, the observed variation was found to be small and nonsystematic for most minerals, except for small differences in mean values of Core and Rim facies of the stock.

It is expectable, therefore, that Rocky Hill data plot in roughly circular areas on the scatter diagrams (Fig. 6). All regressions on these data alone are nonsignificant, but mean values for minerals other than quartz and plagioclase lie very close to the line of best fit to the Cornelia pluton data, and the range of variation among samples occurs within that previously established. We interpret the results positively for our study, the mean-value and degree-of-scatter coincidences with Cornelia regressions for these three phases being the best we could hope to see. Bias in plagioclase results is not unexpected. The Rocky Hill average plot lies approximately as far beneath the calibration curve as the Cornelia test average lies above it. Both reflect the inadequacy of the plagioclase peak, used alone, in estimating concentration. Because quartz estimates are the best among all phases in the Cornelia test, it is disconcerting that the Rocky Hill average plots somewhat off the Cornelia trend. Every Rocky Hill sample has more quartz than the most quartz-rich specimen from the Cornelia pilot-study suite (as judged by optical modes), so that this is extrapolation beyond the limits of the Cornelia data. We attempted to extend the range of the calibration curve by spiking a pilot-study sample with additional quartz powder. The original and spiked calibration curves, however, differed significantly in location where they overlapped. Their difference in slope was in the opposite direction to that required to account for the Rocky Hill results (steeper slope for spiked samples). Available data do not permit a test to determine if the relationship truly becomes nonlinear for higher quartz content, or if the Rocky Hill optical modes or the XRD data contain some unexplained bias. Whereas we hesitate to assign the source of our problem to others, our limited experience suggests that optical modes on sawed slabs tend to overestimate quartz abundance.

The Cornucopia suite exhibits some compositional trends, but includes only 10 samples. Eight are from the tonalite unit of the Cornucopia stock and two are from small satellite plutons (Red Jacket and Last Chance), though all are labeled Cornucopia tonalite here. Because these samples were received in powder form, they were ground differently than all others and appear to be distinctly coarser than our usual material. Taubeneck's (1967) optical modes were derived from at least 2400 points counted over thin section areas of 1500–1700 mm^2. IC numbers average 44 in the interior zone and 56 in the border zone. These data fit the Cornelia-defined regression lines, but they display considerable scatter (Fig. 6). Grinding differences may account for this, but we suspect that optical-mode error may contribute to it as well. We interpret statements in Taubeneck (1967) to indicate determination of IC numbers over 40-mm-long traverses in controlling areas of modal analysis [an unfortunate result fostered by lack of clarity in Chayes (1956) about the traverse lengths used]. If based on traverses 40 mm long, rather than 25 mm, modal error would be nearly twice as large as Taubeneck intended (averaging 2.5–3.0%, rather than 1.5%). Assuming the validity of these two reasons for the larger scatter, we conclude that overall, the Cornucopia results support the applicability of our method.

Figure 7 shows that data from the three plutons conform very well to calibration functions based on


QUARTZ
83%
LOG XRD COUNT
2.76
2.58
2.40
2.22
5
15
25
35
OPTICAL MODE (WT.%)
A
K-FELDSPAR
89%
LOG XRD COUNT
2.18
2.08
1.98
1.88
6
18
30
42
OPTICAL MODE (WT.%)
B
AMPHIBOLE
84%
LOG XRD COUNT
2.30
2.10
1.90
1.70
3
9
15
21
OPTICAL MODE (ARCSINE WT.%)
C
BIOTITE
64%
LOG XRD COUNT
2.96
2.74
2.52
2.30
2
6
10
14
OPTICAL MODE (WT.%)
D
PLAGIOCLASE
54%
LOG XRD COUNT
2.41
2.27
2.13
1.99
26
38
50
62
OPTICAL MODE (WT %)
E

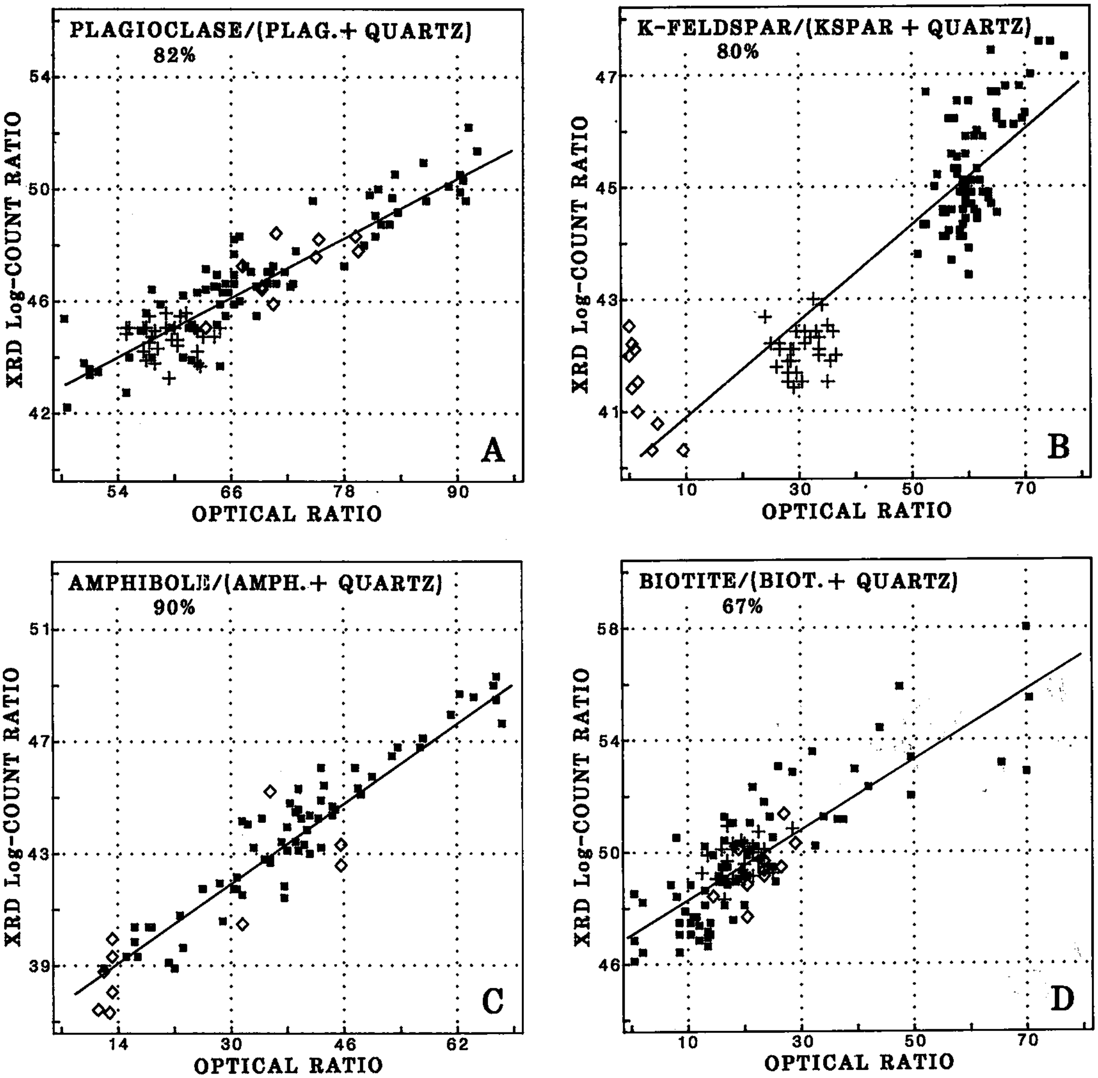


FIG. 7. Scatter diagrams for compound ratios of four phases with quartz; ratios expressed as percentages. Filled squares: Cornelia pluton (n = 75); crosses: Rocky Hill stock (n = 31); open diamonds: Cornucopia tonalite (n = 10). Percentages beneath titles = 100 r^2 for the regression line defined by all 116 samples (in B, note desirability of curvilinear fit; not performed).

FIG. 6. Scatter diagrams for all data from three plutons (n = 116). Filled circles: Cornelia pluton (n = 75); crosses: Rocky Hill stock (n = 31); open diamonds: Cornucopia tonalite (n = 10). Percentages beneath titles = 100 r^2 for regressions defined by all 116 samples.

compound ratios for all phases. A much better fit is achieved for plagioclase (Fig. 7A) and biotite (Fig. 7D) than is obtained for curves based on individual peaks. The calibration for the K-feldspar ratio among all plutons (Fig. 7B) is nonlinear, but the 80% linear fit is a marked improvement over the very poor fit this ratio displays for Cornelia data alone (Table 4). Table 5 presents a more quantitative comparison among all plutons of the methods that produced the best estimates in the Cornelia test. Compound ratios perform better than single-peak intensities for all phases of the Rocky Hill stock (see also Table 4 and Fig. 7). The bias present in estimates from the quartz and plagioclase peaks, noted above, may be the principal cause of this difference from Cornelia pluton results. The Cornucopia tonalite performs more like the Cornelia stock in that single-peak intensities yield the best estimates for biotite, K-feldspar and quartz, with plagioclase derived most accurately from the best-sum procedure. Given the very small quantities of amphibole present in the tonalite, both methods work well for it, though the compound-ratio performance is exceptionally good. Note that all these quantitative comparisons utilize calibrations from the Cornelia pilot-study suite, rather than from all 75 Cornelia samples. This was done to permit exact comparisons among the three test suites. All 116 samples from this study can serve to define calibration curves for further applications in our laboratory (Table 4).

Petrologists reasonably should expect that a new method for modal analysis be able to discriminate among plutons that differ compositionally, and be capable of defining trends in compositional variation within individual plutons. These are two of the most important requirements in the routine petrological study of granites. Figure 8 compares compositional variation for all test-set specimens within and among the three plutons of the study, from modes determined both by optical and XRD methods. The differences that exist between plots of XRD and optical data do not detract significantly from the ability to discriminate among the plutons, or from the definition of compositional variation within each. Whereas there are limitations and weaknesses in the method, as reviewed below, the performance revealed by Figure 8 seems sufficient cause to encourage the application of the method to petrological problems.

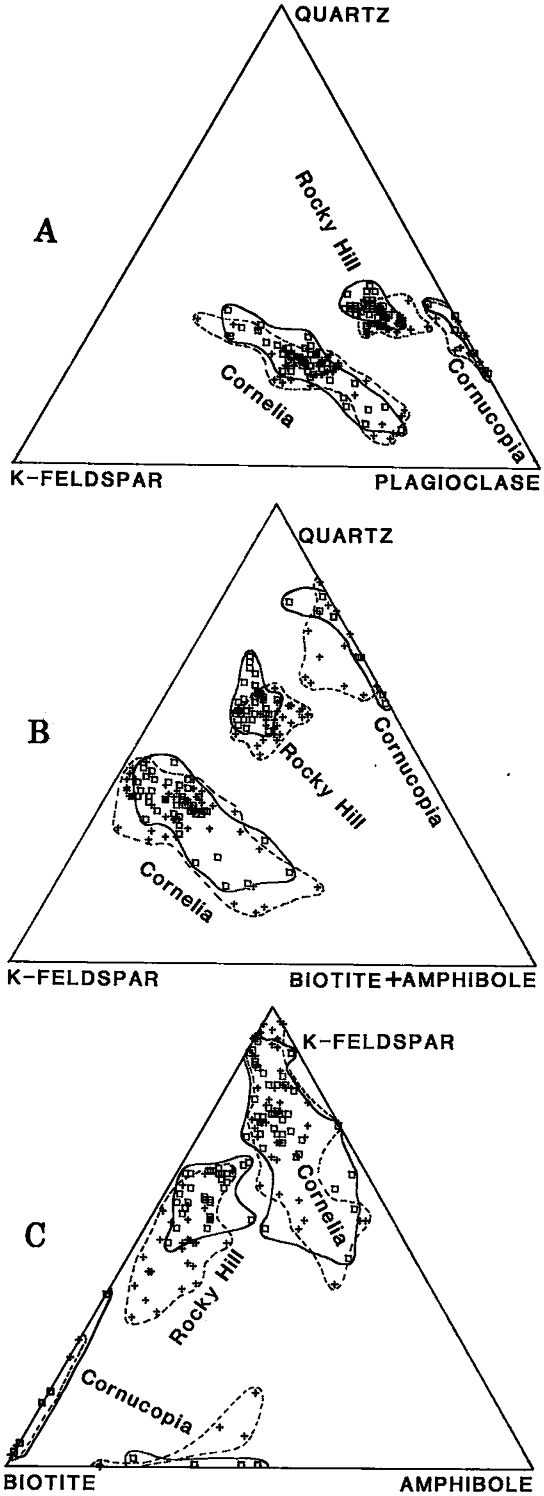


FIG. 8. Comparison of optical and XRD modes for all independent test samples from three plutons (n = 84). XRD modes estimated from Cornelia pilot-study regression functions. For plotting purposes, all Rocky Hill samples were assigned an XRD content of amphibole equal to the optically determined amount (actual content <4% optically; not determined by XRD in this study). Solid lines delineate optical-mode range by pluton (squares: optical-mode plots). Dashed lines and crosses represent XRD-mode range and plots.

DISCUSSION AND SUMMARY OF THE METHOD

Our method can be applied in other laboratories, but the specific calibration functions reported here almost certainly cannot be transported. It is not an ideally general method, but if appropriate optical standards exist at another facility, the procedure can be developed by a process abbreviated from the pilot study reported here. Perhaps the largest barrier to routine adoption of this method is the need for significant numbers of optical modes over a substantial part of the granitic range in developing calibration curves. We have indicated our skepticism about modeling rocks by artificial preparations (except where no choice exists). If optical modes can be determined, a time-saving and potentially effective approach would be to obtain very precise and accurate values for just a few specimens representative of mafic, intermediate and felsic members of a target suite, and to mix their powders to produce a spectrum of standards.

The elements involved in this work that are likely to be generally useful to others are identification of the peaks that are of most value for estimation, demonstration that data transformations can be important means to achieve better fit of calibration functions and more precise estimates, and the comparison among alternate computational schemes in achieving the best estimates for each mineral.

Limitations of the data sets and the scope of investigation should be recognized. None of the rocks used has a visually significant content of muscovite, for example. Where it is abundant, the biotite relationship employed will be affected. Cornelia rocks have abundant orthoclase, but the other plutons have much less K-feldspar. A change in the peak-search range is required if microcline is the K-feldspar species of interest, and further study may be advisable to determine whether the same calibration function serves equally well for both species. Hematite or orthopyroxene (or both) may interfere with the amphibole peak used, a problem that surfaced in four anomalously high values among the 85 samples for which amphibole was determined. Whereas the method's sensitivity extends to contents of 2–3% for three phases, the feldspars probably are not reliably estimated below the 6–10% range. ANOVA studies indicate that sample positioning in the diffractometer is the largest identified source of procedural variance. Therefore, improvement and simplification of the method are most likely to be made by addressing that issue. Addition of a sample spinner probably would improve the outcome in our laboratory.

The recommended method determines the five phases biotite, K-feldspar, plagioclase, amphibole and quartz. Instrument conditions are summarized in Table 1, and statistical expectations, in Tables 4 and 5. Calibration curves from both individual peaks and their compound ratios with the quartz peak (Table 4) must be determined in the laboratory where analysis will be done. Each sample is involved in three instrument runs. The first seeks and counts the peak used for each of the five phases (Table 1). The second (after repositioning of a sample in the holder) counts on four peaks, excluding biotite. The final pass redetermines plagioclase, amphibole and quartz. Taking batch grinding and pressing into account, the maximum time investment in one specimen will be less than 60 minutes.

The concentration of each of the five phases is determined by inverse estimation from average logarithms of the appropriate single-peak intensity. Plagioclase estimation requires computational steps beyond this in order to reduce its relative error to near-equivalence with quartz and K-feldspar; two additional estimates are made. The first of these derives from the compound concentration ratio of plagioclase and quartz, as estimated from its calibration curve, solving it for plagioclase by substitution of the estimated quartz content. The last estimate is derived by forming compound intensity-ratios of all phases with quartz, estimating concentration ratios, and solving simultaneously for concentrations of the five phases. Only the plagioclase result is used. Three analytical sums then exist, which differ owing to the plagioclase estimate used in each, and the plagioclase concentration accepted is the one that makes the sum closest to that expected. Computation may seem laborious when the method is initiated, but is a minor matter thereafter.

This method has the elements we consider to be essential for large-scale, petrological application. Powders can be the same as those used for XRF analysis, a rapid preparation that would be performed in many studies anyway. The total time investment per sample is reasonable, though not insignificant. Finally, the method has been subjected to realistic evaluations of performance. Independent sets of samples from three plutons have been employed in tests, which show that the compositional distinctions among the units, and the compositional trends within each, are approximately as well portrayed from XRD modes as from optical modes. The Cornelia pluton test also demonstrated that the method is able to characterize the compositional differences between a subset of unaltered samples and another having minor hydrothermal alteration. Such capabilities are prominent among those needed by petrologists in the routine compositional analysis of granitic rock bodies.

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