Rapid Modal Analysis of Some Felsic Rocks from Calibrated X-ray Diffraction Patterns

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GEOLOGICAL SURVEY BULLETIN 1209

Prepared in cooperation with the
Nevada Bureau of Mines

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March 3, 1849

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By D. B. TATLOCK

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RAPID MODAL ANALYSIS OF SOME FELSIC ROCKS FROM CALIBRATED X-RAY DIFFRACTION PATTERNS

By D. B. TATLOCK

ABSTRACT

The relationships among diffraction, absorption, and fluorescence allow for reasonably accurate analysis of quartz and other common felsic minerals in many fine-grained rocks, especially altered felsic rocks, from calibrated diffraction patterns of finely ground randomly oriented whole-rock powders, even when scanned at 2° 2θ per minute. Calibration is accomplished by adjusting X-ray tube power until both peak height and background intensities from standard mounts agree consistently with established calibration curves.

No internal standard is used. Instead, significant differences in mass-absorption coefficients (CuKα) of silicate rock matrices—whole rock less mineral analyzed for—are shown to be chiefly a function of iron content. Moreover, iron is the only relatively abundant common rock-forming element whose fluorescence under copper radiation causes appreciable differences in background. Hence, as iron content increases, background intensity increases—thus allowing for an estimate of iron content—and so, too, does the absorptive strength of matrices, which in turn causes differences in peak heights for a given concentration of any mineral to be analyzed for. Modal determinations are made by interpolating between sets of peak height and background curves established from standard powders, consisting preferably of minerals separated from the suite of rocks under study.

Standardized sample preparation is the most important factor in diffraction analysis. The grinding time, per given volume of crushed sample, required to attain a reasonable compromise between optimum reproducibility and maximum intensity of recorded peaks from packed powder mounts is determined experimentally for each group of rocks analyzed.

Groups of quartz determinations compared with normative quartz and with reliable modal counts have standard deviations consistently less than 2.5 weight percent. The indicated accuracy of other common felsic mineral determinations from artificial powders is good. However, in lieu of direct comparison of optical and X-ray modes of natural fine-grained rocks, oxides calculated from X-ray modes have been compared with oxides determined chemically from the same whole-rock powders. These have standard deviations, in weight percent, of 1.6 SiO_2, 1.6 Al_2O_3, 0.7 K_2O, and 0.4 Na_2O.

INTRODUCTION

Chayes (1950) has stated that "the availability of reliable quantitative modal analyses in sufficient number would have immediate and profound effect on petrological theory." Probably few geologists would dispute this. And, indeed, few have done more to advance techniques of modal analysis than has Chayes. But so far, little has been accomplished in developing techniques for the modal analysis of very fine grained rocks—rocks commonly termed aphanitic or cryptocrystalline, and those known to be holocrystalline only because of aggregate polarization (microcryptocrystalline). Judging from the literature, the amount—and probably the accuracy—of modal data on common silicate rocks is almost directly proportional to the grain size of rocks. Without modal analyses, or at least a knowledge of possible relative differences in mineral proportions in rocks of a fine-grained suite, it is difficult to select samples for chemical, or other more detailed, analysis that will show significant differences in composition as a function of either primary or secondary effects.

An attempt is made in this paper to show that, in lieu of point counting, the recording Geiger-counter X-ray diffraction spectrometer can provide reasonably accurate modes of many fine-grained rocks, especially altered felsic rocks, from calibrated patterns of whole-rock powders.

Several workers have described application of the Geiger-counter diffractometer to quantitative analysis of two-component mixtures, or to the determination of one component, usually quartz, in various matrices (Klug and Alexander, 1954, p. 410–439; Jenson, 1951 and 1955). A survey of the literature, however, reveals that the application of X-ray diffraction techniques to the quantitative analysis of silicate rocks has been rather limited. Black (1953) used a direct-counting technique, without an internal standard, in the analysis of bauxite samples on a mass-production basis. Schmalz (1958) employed direct counting, with aluminum as an internal standard, in determining 12 common minerals contained in sediments from the Peru-Chile Trench. Engelhardt and Haussühl (1960) have analyzed coarse-grained granitic rocks with good accuracy, but only on a limited basis.

Although the stability of recent model spectrometers and the reproducibility of peak heights, especially of quartz, have been well demonstrated by many investigators—as, for example, Klug and Alexander (1954) and Weiskirchner (1960)—the use of quantitative diffraction techniques has not been generally employed in petrologic studies, owing largely to the adverse effects of absorption and fluorescence. The time required to counteract these effects by accurately admixing an internal standard to several hundred samples can be prohibitive. In lieu of an internal standard, an attempt is made to show that the relationships between diffraction, absorption, fluorescence, and possibly density do, in fact, permit reasonably accurate and rapid estimates of many common felsic minerals, especially quartz, from recorded patterns of whole-rock powders scanned at 2° 2θ per minute. The analysis of argillic phases in altered silicate rocks is not included, because quantification of clay minerals involves a different and rather specialized approach.

This paper is an elaboration of an earlier progress report (Tatlock, 1961). Most of the analytical data presented were obtained during a study of fine-grained altered felsic rocks of the Permian and Triassic Koipato Group in northwestern Nevada.

The writer gratefully acknowledges many helpful and fruitful discussions with several colleagues, particularly R. A. Gulbrandsen on X-ray procedures, R. G. Coleman on mineral-separation techniques, and E. M. Shoemaker on statistical analysis. The wholehearted encouragement and cooperation of R. E. Wallace and N. J. Silberling in the sampling of the volcanic pile of the Koipato Group is greatly appreciated. The study was made as part of a cooperative project with the Nevada Bureau of Mines.

BASIC ASPECTS OF PROCEDURE

As in all quantitative techniques, diffraction analysis of whole-rock powers from automatically recorded patterns requires that all steps in sample preparation and instrumentation be as nearly standardized as possible.

The technique utilizes the principle that each common rock-forming mineral in a holocrystalline silicate rock produces its own characteristic diffraction pattern independently of the others and that the relative intensities of the patterns are related to the proportions of the minerals present. In practice, the average recorded height of one prominent reflection from each mineral is usually sufficient for modal estimates, provided the instrument has been calibrated with standard powder samples to agree with established intensity-concentration curves and provided no significant superposition by peaks of other constituents is encountered. Corrections must be made, however, for differences in mass absorption and background intensity. Furthermore, sample powders must be properly prepared and mounted so as to reflect reproducible peaks of near-maximum intensity from randomly oriented crystallites that have been ground fine enough to reduce extinction and microabsorption effects to a negligible level.

These basic aspects of quantitative diffraction analysis have been clearly discussed by Klug and Alexander (1954, especially pp. 92–98, 129–130, 252, 290–317, 410–439, 586–587, 677) and by Cullity (1956).

All the quantitative work discussed in this paper has been done with two recent-model Philips Geiger-counter X-ray diffraction spectrometers using copper radiation, nickel filter, and a scanning speed of 2° 2θ per minute at the following instrument settings:

Tube: Approximately 44 kv and 14 ma; set by calibration with standard powders;
Counter: 400 cps full-scale deflection, time constant 4 seconds, 1-degree divergence and antiscatter slits; 0.006 inch receiving slit;
Chart speed: ½ inch per minute.

All samples were mounted in aluminum holders as flat-surfaced powder cakes measuring $1 \times 2 \times 0.16$ cm.

The details of sample preparation, instrumentation, calibration, and selection of lines for measurement are described at the end of this paper.

REPRODUCIBILITY, INTENSITY, AND CRYSTALLITE SIZE

The stability of, and reproducibility attainable with, recent-model spectrometers by automatic recording is generally excellent. Instrument stability can be checked, after a thorough warm-up period, by running a series of peak-height measurements on a single finely ground powder mount without disturbing the mount or the controls of the X-ray generator and circuit panel. The two Philips spectrometers used in the present study invariably record, from an undisturbed finely ground quartz-bearing sample, a mean deviation of less than one-tenth inch from the average of four or more runs across the 4.26–A quartz line at a scanning speed of 2° 2θ per minute. This is largely a test of the stability of X-ray production and of the pulse-integrating circuit, as all effects due to the sample powder are kept constant.

In quantitative work, however, effects due to the sample powder are of paramount importance. Maximum peak intensity, at fixed instrument settings, as well as peak-height reproducibility is required. Reproducibility of peak heights on several mounts of the same sample powder is dependent chiefly on random orientation of crystallites, and random orientation is most nearly achieved in powders of extremely fine crystallite size (Birks, 1945). Moreover, maximum peak intensity, also, is dependent on fine crystallite size.

Alexander, Klug, and Kummer (1948) and Klug and Alexander (1954, p. 292) have demonstrated statistically the relationship between peak intensity, reproducibility, and crystallite size. They prepared four quartz-powder fractions containing crystallites of 15–50, 5–50, 5–15, and <5 microns mean dimensions. The peak intensities of 10 different samples of each fraction were measured under as nearly identical conditions as possible. Figure 1 shows that the reproducibility of intensity measurements from the finer fractions (<15

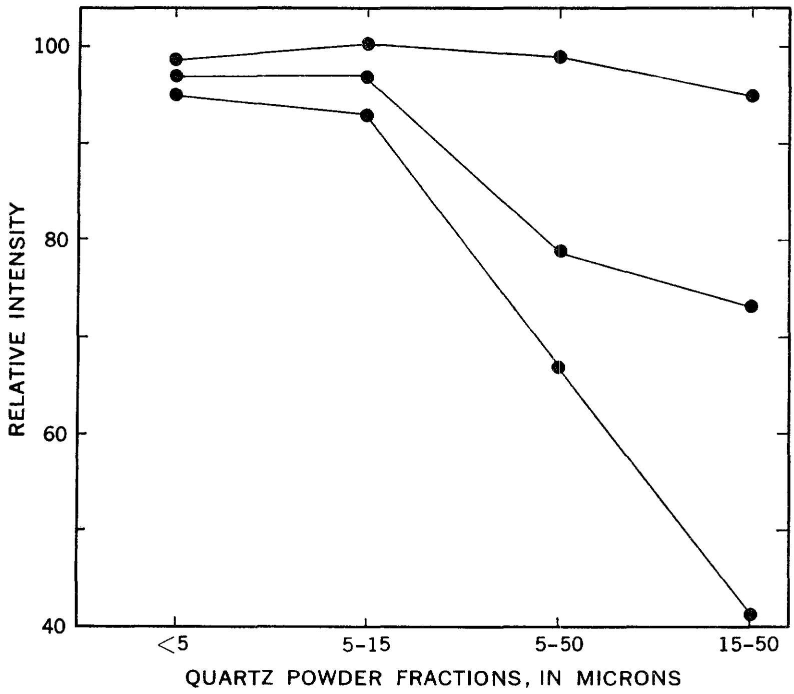

FIGURE 1.—Maximum, minimum, and mean relative intensities from measurements on 10 different mounts of each of four quartz-powder fractions at 3.34 A. Modified from Alexander, Klug, and Kummer (1948).

microns) is considerably better than from the coarser fractions. It shows also that the average observed intensity is greater for the finer fractions, an effect which is attributed to a reduction in extinction in sample powders made up of very small crystallites (Brindley, 1945; Klug and Alexander, 1954, p. 129, 295).

It can be said, therefore, that reproducibility of peak heights for quartz is dependent on random orientation of crystallites, and that random orientation is most nearly achieved in sample powders of very fine particle size; fine particle size reduces extinction and microabsorption effects (Brindley, 1945) to a negligible level and, hence, allows for near-maximum peak intensity.

More recently, however, several investigators (Nagelschmidt, Gordon, and Griffin, 1952; Gordon and Harris, 1955; Brindley and Udagawa, 1959) have shown that diffracted intensity for quartz particles ground smaller than about 2 microns is appreciably diminished owing probably to a thin layer of "amorphous" material on the particle surfaces, developed during grinding, which contributes to X-ray absorption. Weiskirchner (1960) has found a similar reduction in intensities from calcite and quartz (fig. 2), and Engelhardt and Haussühl (1960) from adularia, muscovite and quartz, if crystallite sizes are less than about 2 microns. All investigators agree, however, that for crystallites larger than 30 to 40 microns the phenomenon of extinction severely reduces intensities.

In quantitative diffraction analysis, therefore, to attain both optimum reproducibility and near-maximum intensity, experimental work on sized fractions of pure minerals indicates that sample powders should have a maximum crystallite size of less than 40 microns and a minimum size greater than 2 microns. Obviously, however, any attempt to size-fraction a whole-rock powder to fit this optimum size range will render the sample unrepresentative. Quantitative analysis of a multicomponent mixture requires that all the sample be analyzed, not merely a given size fraction. Since a wide range in particle size is inevitable in preparing whole-rock powders, a compromise between maximum peak intensity and peak-height reproducibility must be attained.

OPTIMUM PARTICLE SIZE VERSUS GRINDING TIME

Considering the grinding equipment generally available in geologic laboratories at the present time, the only practical way to prepare a large number of whole-rock sample powders in a reasonable time is with power mortars. During grinding, a wide range in particle sizes is produced—a range greater than the optimum 2 to 40 microns suggested by the work of Weiskirchner (1960) and others. The maximum optimum particle size can, of course, be controlled by prolonged grinding, but during the process a very fine fraction, submicron in size and certainly less than the minimum optimum size of 2 microns, is inevitably produced. Any attempt to eliminate this very fine material by size-fractioning will amost certainly render the sample unrepresentative.

It should be pointed out that, strictly speaking, particle size and crystallite size are different. A particle may be made up of one or more crystallites. In sample powders prepared from such coarse-grained rocks as granites, particles are commonly single crystallites, whereas in powders of very fine grained rocks, particles may consist of several minute crystallites. The finer the crystallite size, the better the reproducibility of diffraction patterns, but ultimately always at the expense of intensity of peak heights.

To attain a compromise between intensity and reproducibility in the processing of a large number of samples, an attempt was made to relate grinding time per given amount of whole-rock sample to both peak height reproducibility and peak intensity (fig. 3). About 30 grams of microcrystalline nonporphyritic altered rhyolite was

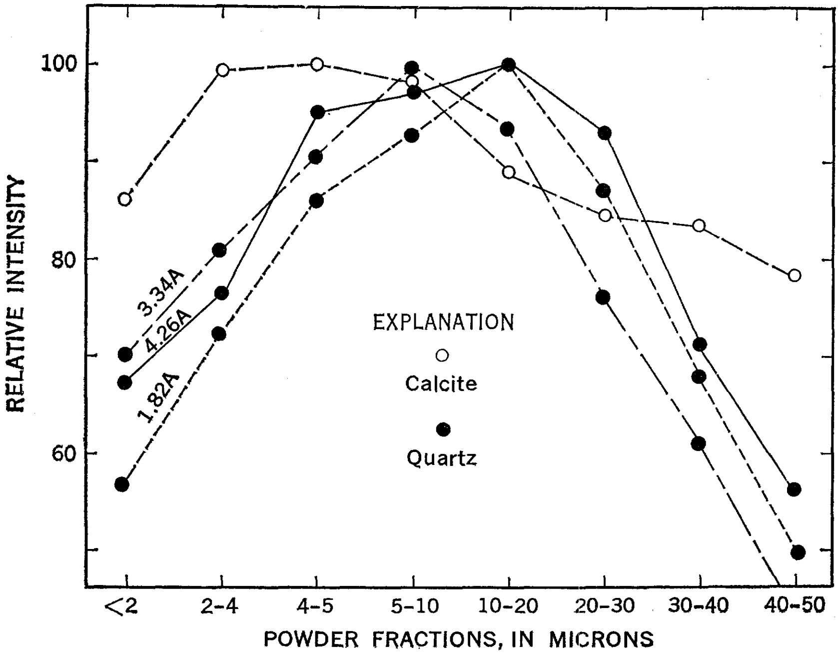

FIGURE 2.—Mean relative intensities from various-sized powder fractions of calcite measured at 3.03 A and quartz at 1.82 A, 3.34 A, and 4.26 A. Modified from Weiskirchner (1960).

crushed in a hardened steel mortar to pass a 1-mm sieve. Sixteen splits of about 1 cc were obtained with the aid of a microsplitter. Each split was ground in a power mortar for periods ranging from 2 to 120 minutes as indicated in figure 3. Ten powder cake mounts of each ground split were scanned, always in the same direction, at 2° 2θ per minute across the quartz, albite, microcline, and muscovite lines at 4.26 A, 3.20 A, 3.25 A, and 10.00 A, respectively. The maximum, minimum, and mean relative intensities recorded from the 10 runs of each of the 16 splits are plotted in figure 3. The curves show that reproducibility improves with increase in grinding time, but at the expense of intensity—except for quartz whose intensity remains nearly constant. The curves are at near-maximum intensity between 10 and 30 minutes of grinding time. Muscovite shows the most abrupt drop in intensity with prolonged grinding.

The experiment was repeated on two other microcrystalline altered felsic rocks, but this time only 11 splits were prepared, and only 6 mounts of each split were scanned. The rocks contained the same constituents as the sample used in preparing figure 3, but in different proportions. Both showed variations in mean relative intensities nearly identical to those shown in figure 3.

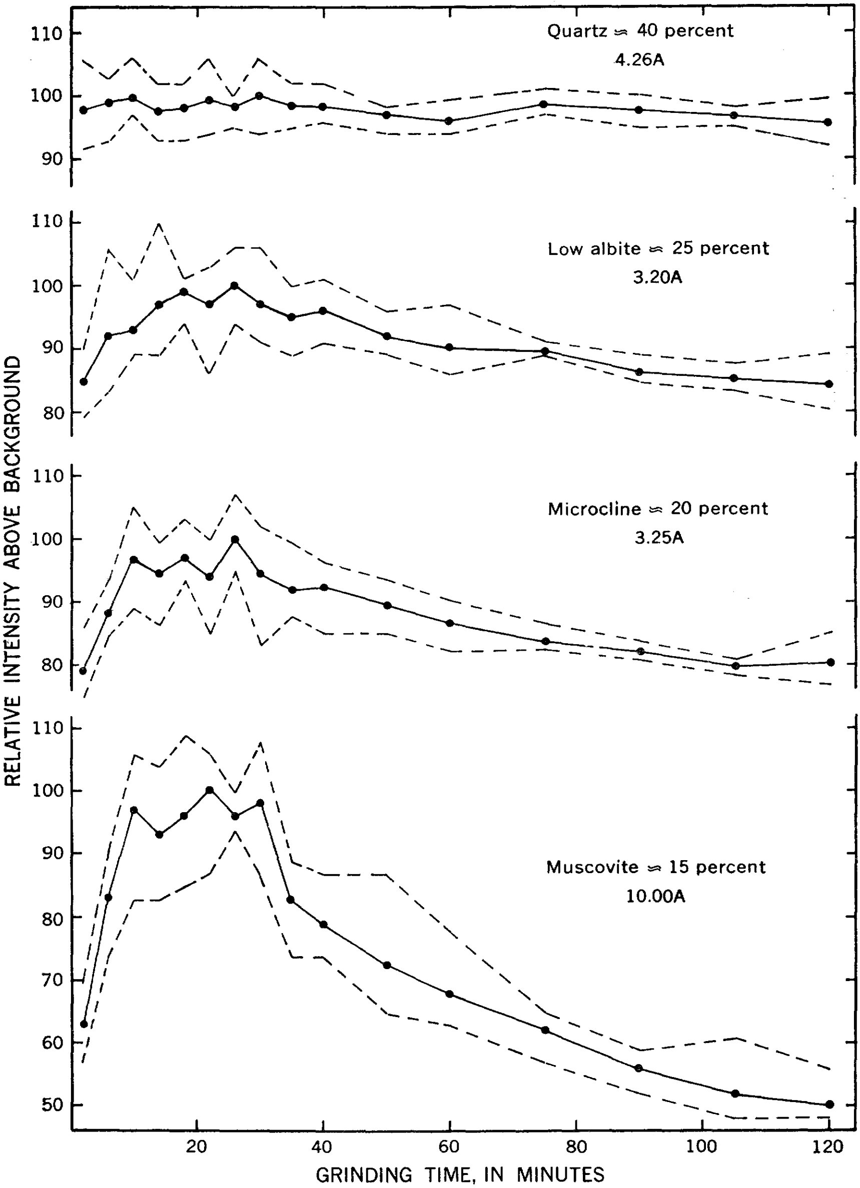

FIGURE 3.—Maximum, minimum, and mean relative peak intensities recorded from 10 different mounts of each of 16 whole-rock powders ground from 2 to 120 minutes and scanned at 2° 2θ per minute. The 16 powders were split, before final grinding, from a single crushed sample of microcrystalline altered rhyolite that had passed a 1-mm sieve. All splits about 1 cc.

Similar experiments performed on three medium-grained granitic rocks indicated that only quartz could be determined quantitatively with reasonable accuracy. Satisfactory reproducibility of feldspar and mica peaks was attained only after a minimum of 40 minutes of grinding (1 cc of crushed sample), at which point intensities had decreased 50 percent.

Summarizing, quantitative diffraction analysis of whole-rock powders is most satisfactory when performed on microcrystalline rocks in which the crystallite size of all constituents is less than about 100 microns. Crushed samples of rocks of this grain size, or finer, can be readily ground in a power mortar to the maximum optimum crystallite size of 40 microns in 15 to 30 minutes. Longer grinding will improve reproducibility but at the expense of intensity, especially of mica. Coarse-grained rocks are less amenable to diffraction analysis because of grinding difficulties that prevent a reasonable compromise between intensity and reproducibility of peak heights.

PRECISION TEST AT HIGH SCANNING SPEED

A typical test of reproducibility by automatic recording made during the course of routine diffraction analysis of altered rhyolites is shown in table 1 and figure 4. A sample of about 20 grams was chipped from a hand specimen of extremely fine grained sparsely porphyritic altered rhyolite and crushed in a hardened steel mortar to pass a 1-mm sieve. The crushed sample was split—with a microsplitter—into four parts and each of the four parts was split to about, but not more than, 1 cc. The four 1-cc splits of crushed sample were then ground for 18 minutes, each in a different mullite power mortar but all of the same model. The largest particles observed under the microscope after grinding were less than 40 microns; it is estimated that at least 70 percent of the powder was less than 20 microns.

Two powder-cake mounts of each of the four finely ground whole-rock powders were prepared. Each of the 8 mounts was scanned from 34° to 6° 2θ at a scanning speed of 2° 2θ per minute on each of two spectrometers. Both instruments were calibrated with standard powder mounts containing 30 and 70 percent quartz to agree with an established intensity-concentration curve. Figure 4 shows that the 4.26 A peak of quartz exhibits slightly better reproducibility than do the muscovite and feldspar peaks. This is chiefly because quartz has no preferential cleavage and, hence, in finely ground powders tends to orient randomly. The reproducibility of the muscovite and feldspar peaks, considering the tendency of these minerals to orient preferentially, is better than might be expected owing largely to fine grinding and to the original extremely fine crystallite size of these minerals in the natural rock. Also, minute mica plates tend to be held more nearly at random by the high percentage of interspersed quartz and feldspar crystallites in the sample powder.

TABLE 1.—*Reproducibility of peak heights on 16 diffraction patterns*

[Recorded from two mounts of each of four whole-rock powders scanned at 2° 2*θ* per minute on each of two calibrated Philips diffractometers. The four powders were split originally from a single crushed sample of altered rhyolite, then ground for 18 minutes. Peak heights are in inches ×10]

	Powder split No.	Quartz 4.26 A	Muscovite 10.00 A	K-feldspar 3.25 A	Albite 3.20 A
Peak height above background, diffraction unit A	1a	47	21	61	59
	b	46	21	61	59
	2a	48	23	57	54
	b	45	20	57	56
	3a	47	20	57	58
	b	48	20	59	56
	4a	46	25	58	58
	b	47	23	58	56
Peak height above background, diffraction unit B	1a	49	22	62	58
	b	46	20	61	62
	2a	48	20	57	56
	b	47	22	61	55
	3a	47	19	55	57
	b	49	21	54	57
	4a	48	25	59	58
	b	47	24	58	55
Average of units A and B		47.2	21.6	58.4	57.1
Range in peak heights		45–49	19–25	54–62	54–62
Standard deviation		1.1	1.9	2.3	2.0
Relative deviation percent		2.3	8.8	3.9	3.5
Range in weight percent of constituent as determined from peak heights		40–43	16–19	15–17	27–31
Weight percent determined from average peak height		41	17	16	28

Reproducibility at a scanning speed of 1° per minute was not measurably better than at 2° per minute. The phenomenon of "undershoot" (Klug and Alexander, 1954, p. 305–308) is not a problem so long as reproducibility is readily attainable.

The relatively high degree of reproducibility attainable from several powders of a given sample scanned on two different spectrometers does not necessarily guarantee accuracy. Accuracy requires that peaks as near maximum intensity as possible be recorded for a given concentration at a fixed setting of the instrument. That the pattern (fig. 4) is near maximum intensity (and hence, the sample powder near optimum crystallite size) is suggested by the fact the sum of the four chief constituents as read from their respective intensity-concentration curves (figs. 11 and 16) is 102 percent (table 1), comparing favorably with a total of about 98 percent as calculated from chemical analyses of similar rocks (table 4).

MASS ABSORPTION AND PEAK INTENSITIES

Although the reproducibility of peak heights on automatically recorded diffraction patterns of whole-rock powders has been shown to be within the limits required for reasonably accurate modal analysis, it remains necessary to correct for differences in the mass-absorption coefficients of the various constituents.

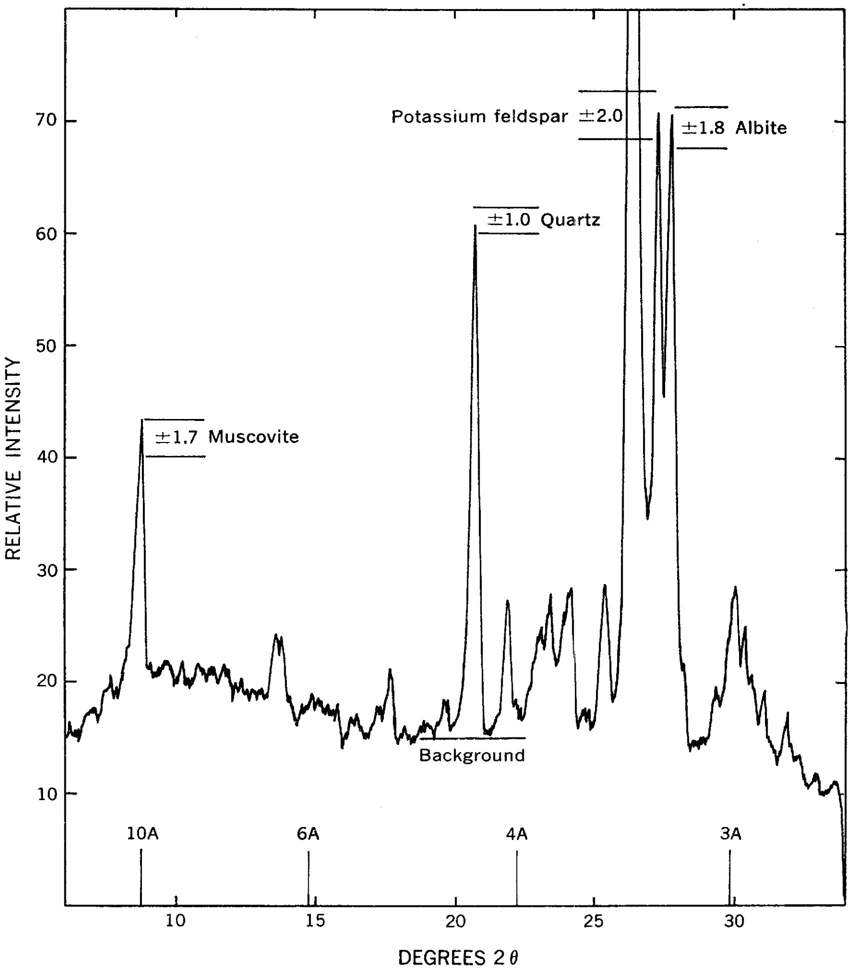

FIGURE 4.—Calibrated diffraction pattern of a whole-rock powder (altered rhyolite) scanned at 2° 2θ per minute, showing the mean deviation of quartz, muscovite, and feldspar peak heights measured from eight different mounts made from four different powders of the same sample and scanned on each of two Philips diffractometers.

In comparing diffraction patterns of whole-rock powders ranging from felsic to mafic in composition, absorption effects are present that usually prevent a direct comparison of the peak heights of any given mineral as a function of its weight concentration. Specifically, when a mixture contains both a weak and a strong absorber, peaks of the weakly absorbing component appear weaker and those of the strongly absorbing component stronger, than expected from a linear relationship for each component (Klug and Alexander, 1954,

p. 92, 411). In multicomponent mixtures, sample powders may be regarded as consisting of just two components, the mineral to be analyzed for, and the sum of the other minerals which may be designated the matrix (Klug and Alexander, 1954, p. 412). The effects of absorption differences on quartz-peak intensities is shown in figure 5, which compares theoretical intensity-concentration curves for quartz mixed with, in order of increasing absorptive strength, (1) magnesite, (2) albite, (3) a hypothetical felsic matrix, (4) a hypothetical mafic matrix, and (5) magnetite. These have mass-absorption coefficients of 20, 34, 48, 75, and 238, respectively, compared with 35 for quartz (table 2). The expression for the theoretical curves is given by Klug and Alexander (1954, p. 411–415):

$$\frac{I_1}{(I_1)_0}=\frac{X_1\mu 1^*}{X_1(\mu 1^*-\mu 2^*)+\mu 2^*}$$

where $(I_1)_0$ is the intensity from the pure component to be analyzed for; I_1 is the intensity of the component when mixed with the matrix; X_1 is the weight fraction of the component; $\mu 1^*$ is the mass-absorption coefficient of the component; and $\mu 2^*$ is the mass-absorption coefficient of the matrix. In almost all silicate rocks, theoretical intensity-concentration curves for quartz will fall between the quartz-albite and the quartz-mafic matrix curves of figure 5.

TABLE 2.—*Mass-absorption coefficients* (CuKα) *of some common oxides and normative minerals*

[Calculated from Internationale Tabellen zur Bestimmung von Kristallstrucktaren, Gebrüder Borntraeger, Berlin, 1935]

Oxides	*MAC*	*Minerals*	*MAC*
SiO_2	35	Orthoclase	49
Al_2O_3	32	Albite	34
Fe_2O_3	231	Anorthite	52
FeO	255	Nephelite	32
MnO	223	Acmite	102
MgO	30	$CaSiO_3$	79
CaO	127	$MgSiO_3$	33
Na_2O	26	$FeSiO_3$	155
K_2O	121	Mg_2SiO_4	32
H_2O	11	Fe_2SiO_4	190
TiO_2	127	Magnetite	238
P_2O_5	39	Ilmenite	189
CO_2	11	Apatite	89
Iron	324	Calcite	74

MASS ABSORPTION AND IRON CONTENT

The usual procedure for countering absorption effects in multicomponent mixtures is to add an internal standard (Klug and Alexander, 1954, p. 426), but the admixing of the reference material is time consuming, dilutes the sample, and increases the number of measurements required. A more direct procedure may be employed, similar in part to the diffraction-absorption technique of Leroux, Lennox, and Kay (1953), and to that of Black (1953) in his analysis

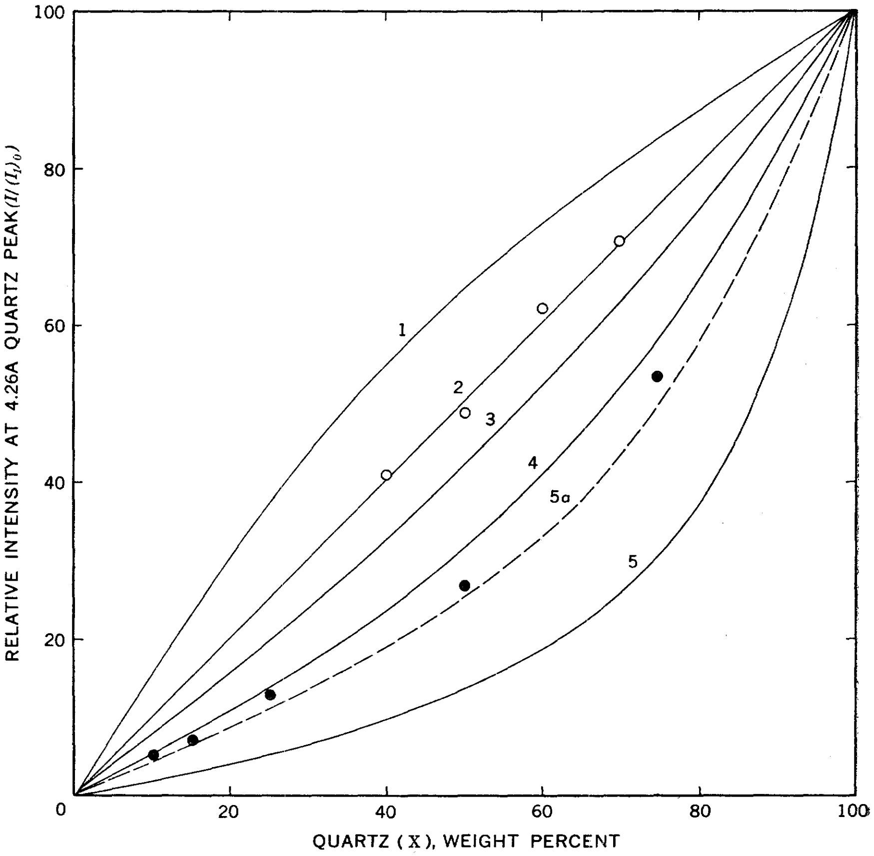

FIGURE 5.—Comparison of theoretical intensity-concentration curves for quartz mixed with (1) magnesite, (2) albite, (3) felsic matrix, (4) mafic matrix, and (5) magnetite. Experimental measurements for some quartz-albite (open circles) and quartz-magnetite (solid circles) mixtures are shown. Dashed curve (5a) is quartz-magnetite curve corrected for density differences.

of bauxite samples. The procedure is based on the premise that iron is the element chiefly responsible for appreciable differences in mass absorption in silicate rocks, and also that iron is the only relatively abundant common rock-forming element whose fluorescence under copper radiation effects appreciable differences in background, thus allowing for measurement of iron content.

That iron is, indeed, the element responsible for appreciable differences in absorption in silicate rocks is suggested by the mass-absorption coefficients (MAC) of some common oxides and normative minerals listed in table 2. Although MnO and TiO_2 have high coefficients, their effect on average mass absorption is small owing to their low concentrations in average rocks. The high coefficients of

CaO and K_2O tend to balance one another in rocks ranging from felsic to mafic.

As stated earlier, sample powders of silicate rocks may be regarded as consisting of just two components, the mineral to be analyzed for, and the sum of the other minerals which may be designated the matrix. Regardless of which of the chief felsic minerals is analyzed for in rocks ranging from felsic to mafic, the MAC's of matrices, excluding iron, will remain nearly constant; with iron included, the MAC's of matrices will show a regular variation with iron content.

To demonstrate the relationship of iron to absorption differences, it will be assumed that the weight concentrations of quartz and plagioclase are to be determined in rocks ranging from felsic to mafic in composition. The mass-absorption coefficients of quartz-free matrices and of plagioclase-free matrices of 18 average igneous rocks (Nockolds, 1954), as well as G-1 granite and W-1 diabase (Fleischer and Stevens, 1962), have been calculated, both with and without iron (table 3), from the MAC's of oxides and normative minerals in table 2. In analyzing for quartz, table 3 and figure 6 show that the

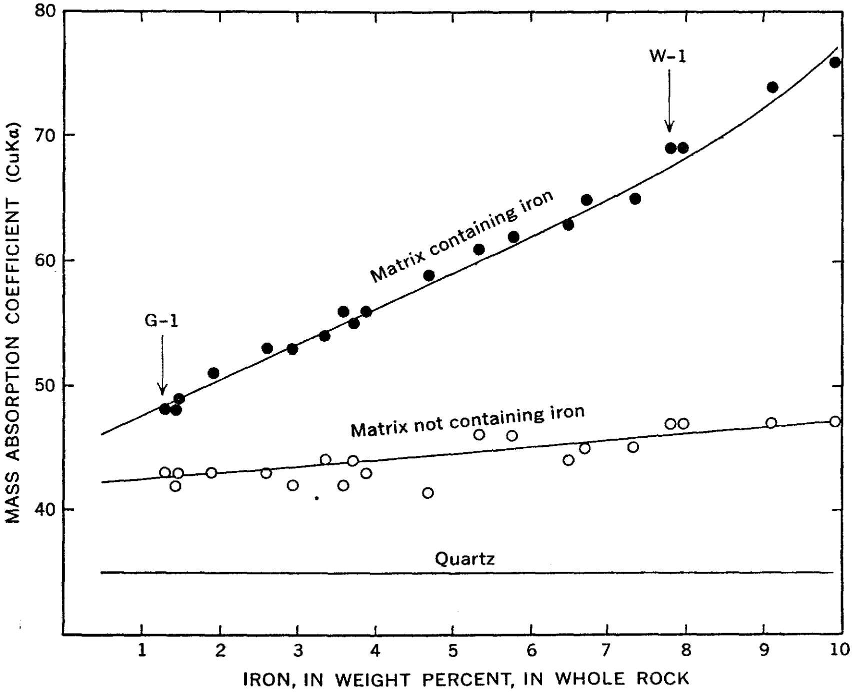

FIGURE 6.—Variation of mass-absorption coefficients of matrices—whole rock less normative quartz—of average igneous rocks (Nockolds, 1954) as a function of iron content (solid circles) and without iron (open circles). Plotted values are those of rocks listed in table 3.

MAC's of the matrix portion—whole rock less normative quartz—of average igneous rocks, exclusive of iron, are nearly constant, ranging from 42 for alkali granite to 47 for tholeiitic andesite and tholeiitic basalt. With iron included in the matrices, however, the MAC's range from 48 for alkali granite to 76 for tholeiitic andesite.

TABLE 3.—*Total iron, normative quartz and plagioclase, and mass-absorption coefficients* (CuKα) *of quartz-free and plagioclase-free matrices, both with and without iron, of some average igneous rocks*

[Adapted from Nockolds, 1954. Total Fe is 0.70 (Fe_2O_3)+0.78 (FeO)]

Rock name	Quartz				Plagioclase				
	Total Fe	Norm. quartz MAC 35	MAC of quartz-free matrix		Norm. plag.	An content	MAC plag.	MAC of plagioclase-free matrix	
			Matrix less Fe	Total matrix				Matrix less Fe	Total matrix
G-1 granite	1.37	28.6	43	48	33.7	16	37	42	48
Alkali granite	1.43	32.2	42	48	32.1	9	36	42	48
Calc-alkali rhyolite	1.45	33.2	43	49	30.1	17	37	42	48
Calc-alkali granite	1.90	29.2	43	51	31.8	18	37	43	51
Adamellite	2.62	24.8	43	53	39.4	28	39	43	55
Granodiorite	2.96	21.9	42	53	48.9	34	40	42	58
Calc-alkali trachyte	3.35	--------	44	54	38.5	25	39	48	65
Tonalite	3.61	24.1	42	56	53.8	39	41	40	63
Calc-alkali syenite	3.73	2.0	44	55	43.0	23	38	50	68
Dacite	3.90	19.6	43	56	57.4	41	41	41	68
Peralkaline granite	4.70	26.2	41	59	34.6	0	34	42	63
Monzonite	5.36	--------	46	61	45.1	35	40	51	78
Latite	5.78	.5	46	62	47.0	41	41	50	81
Mangerite	6.47	2.0	44	63	53.0	40	41	49	87
Andesite	6.71	5.7	45	65	58.1	47	42	47	92
Diorite	7.33	.3	45	65	54.1	48	43	48	93
W-1 diabase	7.79	4.1	47	69	47.6	64	46	47	89
Gabbro	7.95	--------	47	69	53.1	64	46	48	95
Tholeiitic basalt	9.07	3.5	47	74	44.8	58	44	50	96
Tholeiitic andesite	9.93	3.2	47	76	45.3	40	41	52	102

Similarly, in analyzing for plagioclase (table 3 and fig. 7), the MAC's of the matrices—whole rock less normative plagioclase, excluding iron—range from 42 in granite and rhyolite to 52 in tholeiitic andesite; the iron-free matrix curve very nearly parallels that of the normative plagioclases (fig. 7). With iron included in the matrices, the mass-absorption coefficients range from 48 in granites to 102 in tholeiitic andesite. Hence, in analyzing for quartz and plagioclase, iron is shown to be the element chiefly responsible for appreciable differences in mass absorption in the matrix component of the common silicate rocks, and thereby the element that effects differences in quartz and plagioclase peak intensities for a given quartz or plagioclase concentration. Similar effects from iron can be theoretically demonstrated in analyzing for any of the major silicate rock-forming minerals.

IRON, FLUORESCENCE, AND BACKGROUND INTENSITY

When analyzing for quartz and plagioclase in the more common silicate rocks, iron has been shown to be the element chiefly respon-

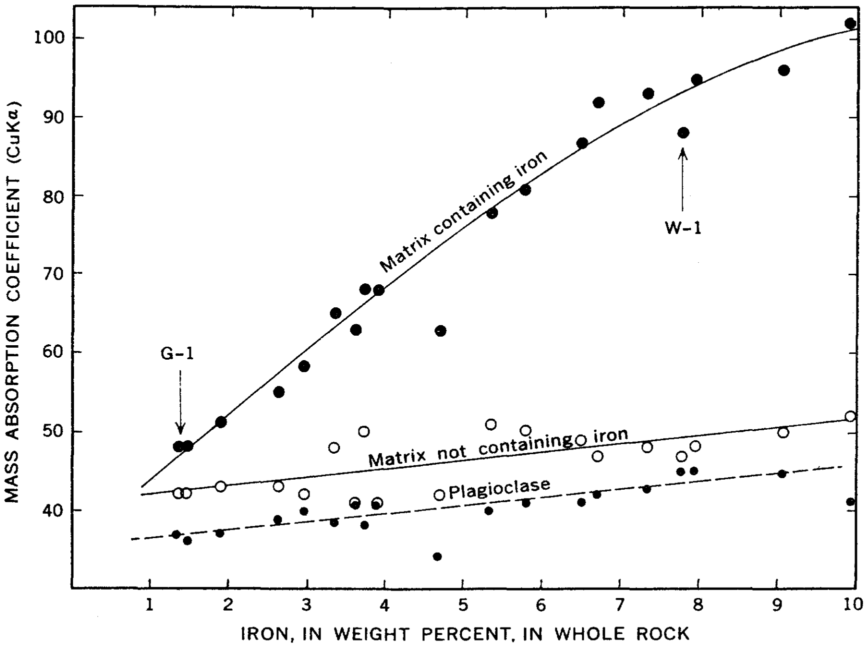

FIGURE 7.—Variation of mass-absorption coefficients of matrices—whole rock less normative plagioclase—of average igneous rocks (Nockolds, 1954) as a function of iron content (solid circles) and without iron (open circles). Dashed curve shows variation of MAC's of normative plagioclase. Rocks are those of table 3.

sible for appreciable differences in absorption. Iron, also, is the only relatively abundant common rock-forming element whose fluorescence (Klug and Alexander, 1954, p. 95) under copper radiation effects appreciable differences in background.[1] The greater the iron content of a holocrystalline whole-rock powder, the greater the background intensity of its diffraction pattern. Experimentally determined background curves for quartz-albite and quartz-magnetite mixtures, using copper radiation, are shown in figure 8 along with two theoretical curves representing felsic and mafic matrices that contain 1.9 and 10.0 percent iron. The relationship between iron content and background intensity allows for an estimation of the total iron in a sample by reading the background at a given angle 2θ after the diffraction unit has been calibrated with standard mounts to agree with established intensity-concentration and background curves (figs. 10 and 11). In figure 9 the total iron—0.70 (Fe_2O_3)+0.78(FeO)—calculated from

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[1] Manganese fluorescence (CuKα) effects differences in background that are about half as great as those due to iron. Manganese content, however, seldom exceeds a few tenths of a percent in common silicate rocks (Nockolds, 1954).

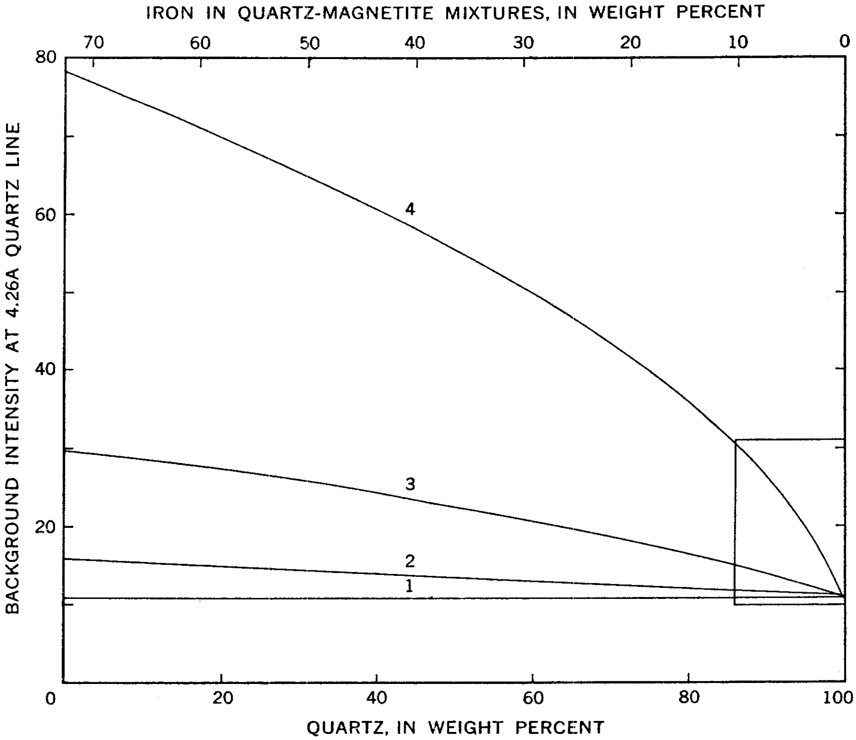

FIGURE 8.—Comparison of background curves for mixtures of quartz and (1) albite, (2) felsic matrix, (3) mafic matrix, (4) magnetite (CuKα; nickel filter). Background measured at 4.26 A quartz line. Variation in curves is chiefly a function of iron content. That portion of the quartz-magnetite curve outlined near the lower right corner is the mirror image of the curve in figure 9.

chemical analyses of altered rhyolitic, andesitic, and basaltic rocks, and graywackes, has been plotted against background intensities at the 4.26 A quartz line as recorded on diffraction patterns of splits of the chemically analysed powders. The background intensity is the average of measurements on both sides of the selected line as shown in figure 4 (Carl, 1947). The curve was constructed from background intensities recorded on weighed mixtures of quartz and pure magnetite, and is actually the mirror image of that portion of the quartz-magnetite curve outlined in the lower right corner of figure 8. The standard deviation of iron determined by background intensity from that determined chemically is about 0.45 weight percent.

POSSIBLE EFFECTS OF DENSITY DIFFERENCES

Theoretically, in correcting for absorption differences, the density of components should have no effect on the position of calculated intensity-concentration curves. This has been shown experimentally

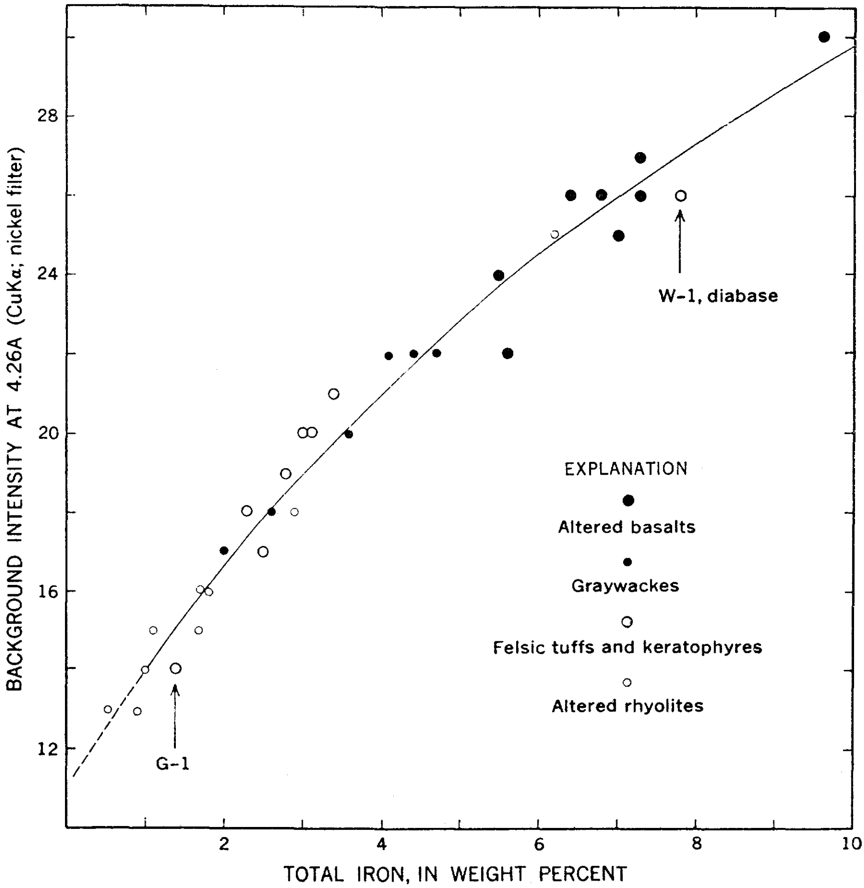

FIGURE 9.—Background intensities, to nearest tenth of an inch, recorded from diffraction patterns of splits of 31 chemically analyzed powders plotted against total iron content. Curve was determined experimentally from quartz-magnetite mixtures.

by Klug and Alexander (1954, p. 414) for quartz mixed with BeO (very low mass absorption, high density) and with KCl (high mass absorption, very low density). Referring again to figure 5, the theoretical curve for quartz-albite mixtures is almost linear and very nearly coincides with some experimentally determined points, as one might expect from the similar mass-absorption coefficients of quartz and albite. In contrast, experimental quartz-magnetite points (fig. 5, solid circles) depart radically from the theoretical curve. This departure probably arises chiefly from microabsorption effects (H. L. Klug, written communication, 1963; Brindley, 1945; and Engelhardt, 1959), which result largely from the gross difference in linear-absorption coefficients (mass-absorption coefficient times density) between quartz and magnetite (93 and 1234, respectively). Microabsorption effects can be rendered negligible only if the product of linear-absorption coefficient and particle diameter is extremely small—smaller than can be attained easily by routine grinding procedures. If the product is large, as in magnetite powders, the X-ray reflection process is confined mainly to a surface layer of particles (Brindley, 1945, p. 350), in which case the difference in specific gravity between quartz and magnetite may affect the position of the experimental curve because of the greater volume percent—and hence, greater percent of surface exposed to radiation—of quartz relative to its weight percent when mixed with a denser material. The relationship is expressed by:

$$Q=\frac{q\rho m}{Q\rho m+m\rho q}$$

where Q is volume percent of the component to be analyzed for; q is weight percent of the component; ρq is specific gravity of the component; m is weight percent of matrix; and ρm is specific gravity of matrix. It is interesting to note, though possibly fortuitous, that if allowance is made for both density and mass-absorption differences, a theoretical quartz-magnetite curve (fig. 5, dashed curve) will nearly coincide with the experimental points. A correction for density differences necessitated by microabsorption effects is probably not required when analyzing for felsic minerals in silicate rocks unless the iron content of the matrix exceeds about 20 percent.

INTENSITY-CONCENTRATION CURVES FOR QUARTZ ANALYSIS

Regardless of possible discrepancies between theoretical and experimental intensity-concentration curves, as displayed by the quartz-magnetite curves of figure 5, direct analysis for quartz remains possible by reference to curves prepared from synthetic mixtures.

To compensate for the absorption and fluorescence effects of iron, four intensity-concentration curves and their corresponding background curves were established from prepared powders of quartz mixed, in order of increasing absorptive strengths, with (a) natural pinite (very fine muscovite-pyrophyllite mixture), (b) biotite-actinolite greenstone, (c) chlorite, and (d) magnetite; the letters correspond with the curve sets in figure 10. The curves are based on the diffraction intensity of copper radiation from the (100) plane of quartz (Weiskirchner, 1960) and the background intensity in the immediate vicinity of the same line (4.26 A or 20.8° 2θ) at a scanning speed of 2° 2θ per minute. The intensity of the X-ray source was adjusted to give almost full deflection of the recording pen at the 70 percent quartz level as this was the maximum quartz content expected in the rocks under study.

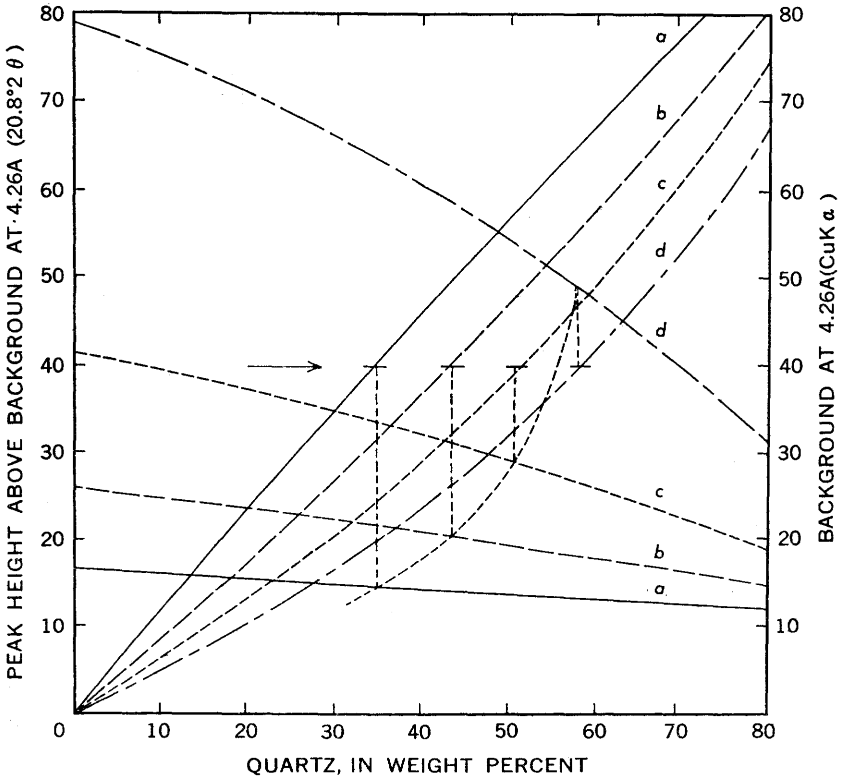

FIGURE 10.—Intensity-concentration curves and corresponding background curves for quartz mixed with matrix materials having different mass-absorption coefficients resulting chiefly from differences in iron content. Construction of interpolation curve is illustrated.

Differences in the mass-absorption coefficients of matrices of common silicate rocks have been shown to be chiefly a function of iron content (fig. 6), and iron content is expressed by background intensity (fig. 9). As iron content increases, background intensity increases, and so, too, does the absorptive strength of the matrix, which has the effect of depressing the peak height, or intensity-concentration, curve. Using this relationship, the quartz content of a rock powder can be determined from any combination of peak height (above background) and background by interpolating between established sets of intensity-concentration and background curves. The greater the mass-absorption coefficient of the matrix—as a function of iron, and expressed by background—the greater the quartz content for a given peak height. For example, in figure 10, at a peak height above background of 40, the quartz content of a powder having the absorption characteristic of curve set *a* would be 35 percent, of curve-set *b* 43 percent, of curve set *c* 51 percent, and of curve set *d* 58 percent. This relationship establishes a so-called interpolation curve, the construction of which is illustrated in figure 10. A series of interpolation curves is shown in figure 11, in conjunction with an intensity-concentration and background curve set. Actually, any one of the sets of curves in figure 10 showing peak height and corresponding background intensity could be used in conjunction with the interpolation curves in preparing figure 11. To illustrate how the weight percent of quartz is determined from figure 11, assume a peak height above background of 50 and a background of 20; both are read in the same units on the ordinate scale. By following the dashed lines, the quartz content for this combination of peak height and background intensities is shown to be 53 percent.

The intensity-concentration and background curve set of figure 11 was developed specifically for determining the quartz content of extremely fine grained altered volcanic rocks of the Koipato Group,

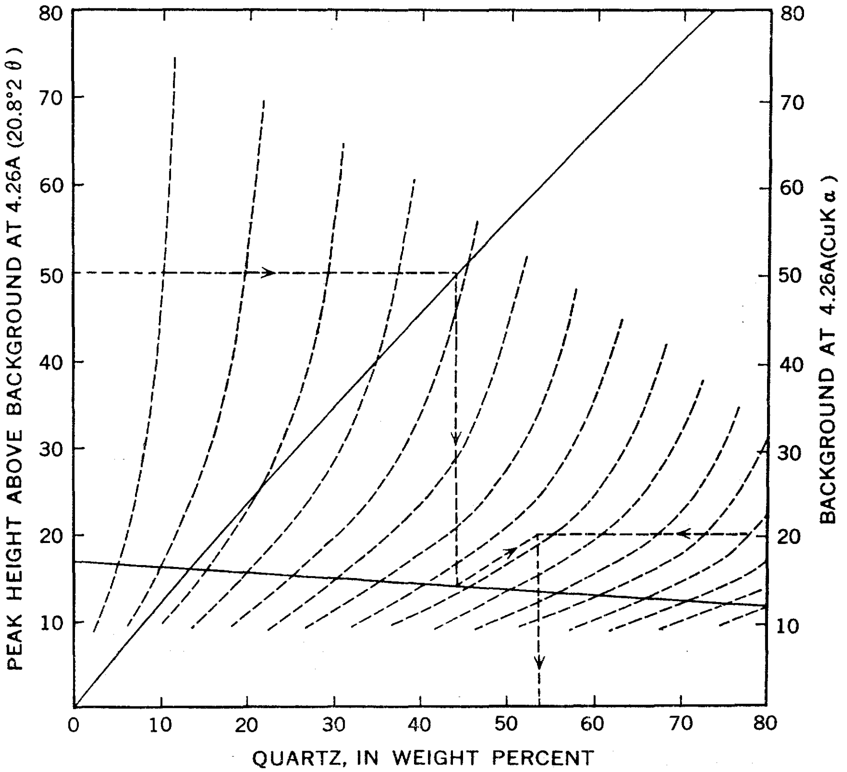

FIGURE 11.—Intensity-concentration and background curve set, with interpolation curves, for determining weight percent of quartz in silicate rocks containing 0 to 72.4 percent iron.

of Permian and Early Triassic age, in northwestern Nevada. A regression curve for quartz calculated from 27 chemically analyzed Koipato rhyolitic rocks (table 4) as a function of X-ray modal quartz determined from diffraction patterns of splits of the analyzed powders is shown in figure 12. The standard deviation is 2.2 weight percent.

The curve set of figure 11, although established for analysis of a given suite of rocks, has been found to give reliable determinations of quartz in almost all common holocrystalline silicate rocks, both fresh and altered, regardless of rock type or source area. Figure 13 shows the weight percent of quartz determined from diffraction patterns of splits of 26 chemically analyzed samples plotted against calculated quartz. The samples consist of 11 granitic rocks (granodiorite and quartz monzonite), 6 felsic graywackes, 4 altered felsic tuffs, and 3 quartz keratophyres from various sources in California and Nevada, as well as G–1 granite and W–1 diabase. The percentage of calculated quartz in the granitic rocks agrees very closely with the percentage of quartz determined from modal counts made on stained slab surfaces. The tuffs, graywackes, and keratophyres

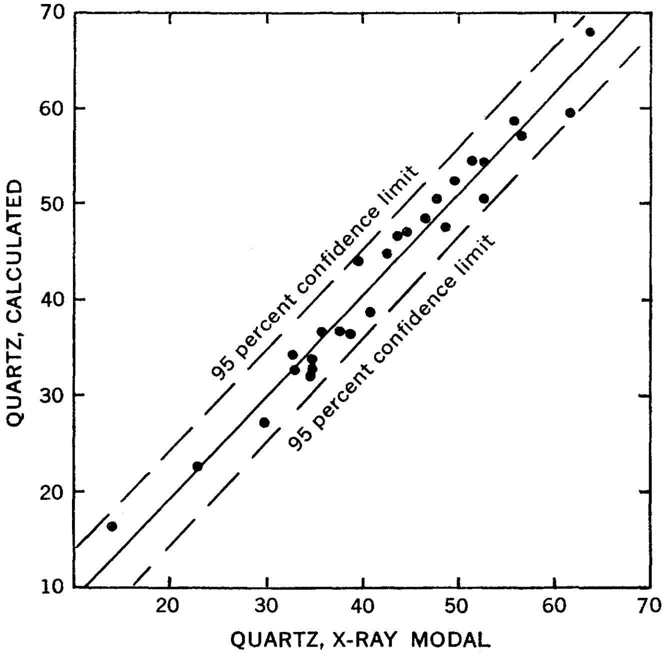

FIGURE 12.—Regression curve of calculated quartz as a function of X-ray modal quartz determined from splits of 27 chemically analyzed samples of rhyolitic rocks from the Koipato Group, Nevada.

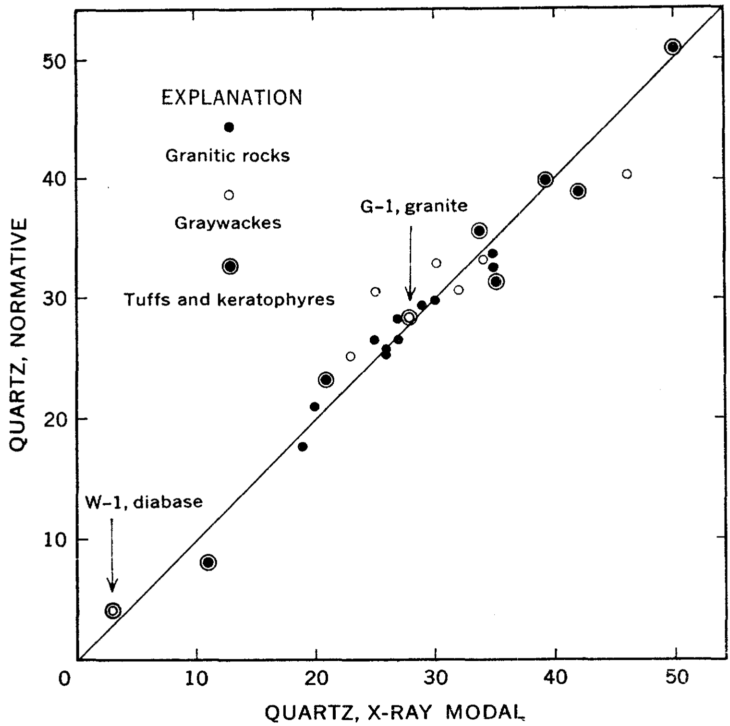

FIGURE 13.—Weight percent of quartz determined from diffraction patterns of splits of 26 chemically analyzed powders plotted against normative quartz.

could not be reliably counted. The standard deviation of the X-ray modal quartz from the calculated quartz is 2.4 weight percent. Considering only the 12 granitic rocks, the standard deviation is 1.2 weight percent.

A comparison of quartz determined from diffraction patterns with thin-section modal quartz is shown in figure 14. Both the X-ray and thin-section determinations were made by Rowland W. Tabor, of the U.S. Geological Survey, on specimens of mica schist and fine-grained gneiss from the Cascade Range, Washington. The open circles are thin-section determinations considered to be less than satisfactory owing to uneven distribution of quartz lenses, difficulties in distinguishing quartz from plagioclase, obscuring by alteration products, or badly plucked sections. In fine-grained altered rocks of this type, modal quartz determined by X-ray is probably more accurate than that determined from thin-section point counts. The standard deviation of the X-ray modal quartz from the thin-section quartz is 4.3 percent, without density corrections. For the seven more reliably counted specimens the standard deviation is 2.2 percent which is about the same as the standard deviations calculated for quartz in rhyolitic rocks of the Koipato Group (fig. 12) and the rocks of figure 13.

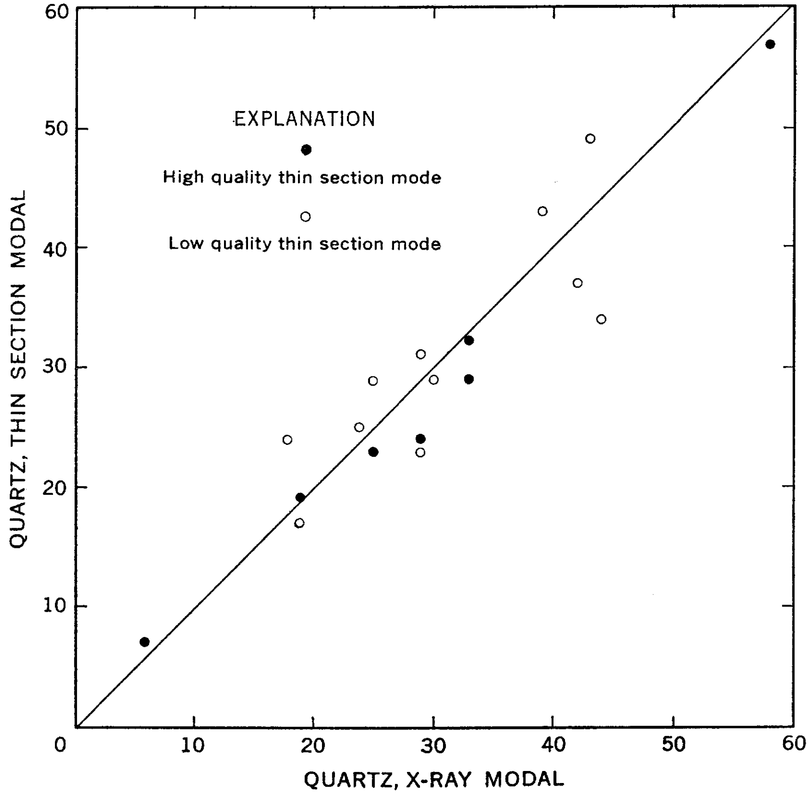

Figure 14.—Weight percent of quartz determined from 18 powder diffraction patterns of schists and fine-grained gneisses plotted against modal quartz determined from thin-section counts.

ROCK CLASSIFICATION FROM QUARTZ AND IRON ANALYSIS

Many igneous rocks can be tentatively classified merely on the basis of their quartz and total-iron contents as determined from calibrated diffraction patterns (figs. 9 and 11). This is shown in figure 15 where theoretical differentiation trends have been drawn through plots of normative quartz versus iron for some average rocks of Nockolds (1954); the rocks are listed in table 3 of this paper.

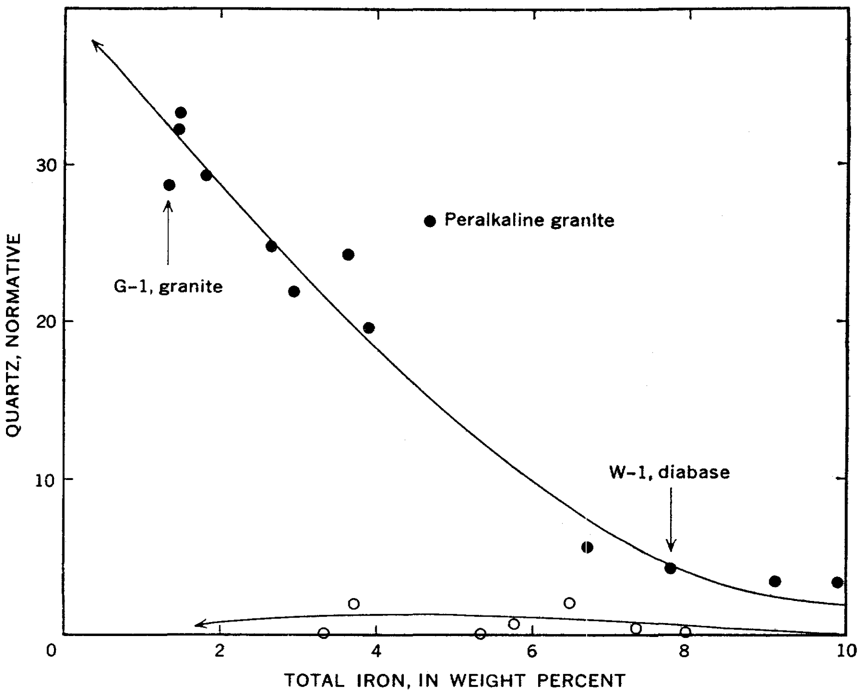

FIGURE 15.—Relationship of theoretical differentiation trends to quartz and iron contents of rocks listed in table 3.

ANALYSIS OF ALTERED RHYOLITIC ROCKS OF THE KOIPATO GROUP, NEVADA

It has been shown that reasonably accurate weight concentrations of quartz and total iron can be readily determined from calibrated powder diffraction patterns of almost all the common holocrystalline silicate rocks (figs. 9, 12, 13, and 14). Quantitative determinations of most other common constituents from diffraction patterns are not universally reliable, however, owing largely to intensity and spacing differences brought about by compositional variations within mineral species. Also, the innately fine crystallite sizes of some minerals, especially the feldspars, in many microcryptocrystalline rocks, commonly reflect broadened peaks of less than maximum intensity (Klug and Alexander, 1954, p. 586).

Nevertheless, in studying rocks of a given type from a given limited area, relative differences in the proportions of the chief felsic constituents are readily determined from calibrated diffraction patterns.

And, going a step further, reasonably accurate quantitative determinations can be obtained by establishing intensity-concentration curves for each of the chief felsic minerals from artificial powder mixtures consisting of constituents separated from the rocks under study.

This has been done in analyzing more than 800 samples of rhyolitic rock from the Kiopato Group, of Permian and Early Triassic age, in northwestern Nevada. The rhyolitic pile consists of flow, pyroclastic, detrital, and intrusive rocks which crop out sporadically over an area of about 3,000 square miles and probably originally aggregated at least 1,000 cubic miles. All the rocks are holocrystalline although extremely fine grained, rendering modal analysis by microscopic methods impossible. Furthermore, the pile is pervasively altered; the alteration is reflected chiefly in wide differences in the proportions of quartz, muscovite, K-feldspar, albite, andalusite, and pyrophyllite. Various combinations of these minerals make up more than 95 percent of the average rock. Feldspar and andalusite-pyrophyllite are everywhere mutually exclusive. Quartz is ubiquitous and generally the most abundant constituent.

Intensity-concentration curves for determining the weight percentages of muscovite, microcline, monoclinic K-feldspar, albite, and andalusite in rhyolites of the Koipato Group are shown in figure 16. Background curves were not established for these minerals, because significant differences in mass absorption in the rhyolites is small owing to their generally low iron content. All the artificial powders from which peak intensities were measured to establish the intensity-concentration curves were made up of constituents separated from rocks of the Koipato Group, usually by centrifuging 20 to 50 micron powders in heavy liquids of appropriate specific gravity. The relatively smooth loci of experimental points determined, in increments of 5 or 10 weight percent, from the artificial powders suggest that the precision of the quantitative diffraction technique is satisfactory. The accuracy of the technique, however, can be checked only indirectly as there is no way possible to measure the absolute weight fraction of each constituent in a fine-grained altered rock.

Table 4 compares X-ray modal analyses, determined from diffraction patterns of splits of chemically analyzed whole-rock powders, with modes calculated from the chemical analyses. The modes have been calculated in a manner similar to the calculation of the CIPW norm except that MgO and the available FeO remaining after ilmenite and magnetite are allotted to biotite or chlorite or both in lieu of pyroxene. The K_2O remaining after biotite and the Al_2O_3 after biotite, chlorite, and plagioclase are apportioned between K-feldspar and muscovite by simultaneous equations, which gives:

$$m=\frac{A-K}{2}$$

$$f=K-m$$

where m is muscovite molecules, f is K-feldspar molecules, A is available Al_2O_3, and K is available K_2O.

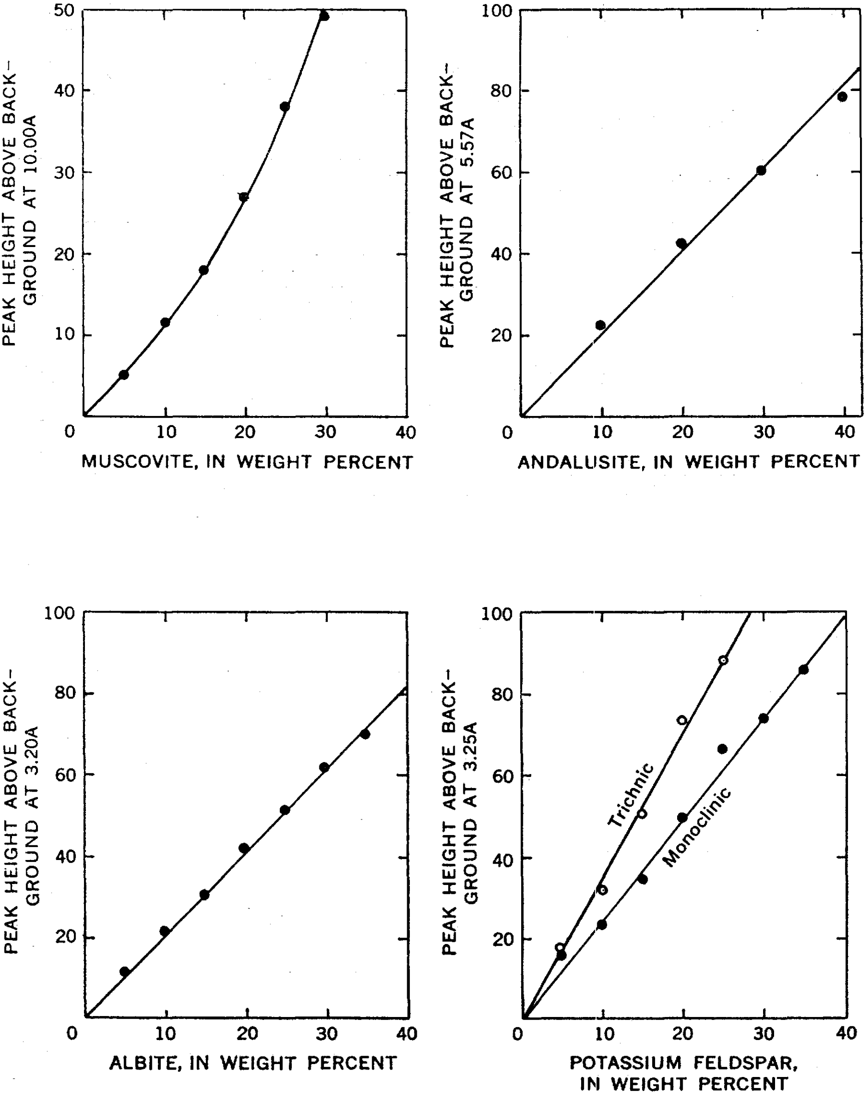

FIGURE 16.—Intensity-concentration curves for determining muscovite, andalusite, albite, and K-feldspar in altered rhyolitic rocks of the Koipato Group, Nevada. Dots and circles are average experimentally determined points used in establishing the curves.

TABLE 4.—*Calculated minerals, modal minerals determined from diffraction patterns,*

[All are in weight percent. Analyses are of

Sample	Calculated minerals						X-ray modal minerals			
	Q	M	Kf	Ab	Sub-total	Other	Q	M	Kf	Ab
1	38.6	7.1	21.1	31.4	98.2		41	11	18	28
10	44.8	13.6	38.9	1.6	98.9		43	13	42	------
46	54.4	20.0	22.2	1.1	97.7	An, 1.1	53	18	27	------
58	57.2	27.6	3.3	9.4	97.5	Hm, 1.0	57	28	------	12
58F	58.6	20.2	7.2	12.1	98.1	Hm, 1.3	56	25	4	12
61B	27.1	1.7	------	67.6	96.4	Kaolinite, 2.3	30	2	------	65
61W	22.7	23.5	31.7	18.3	96.2	Cc, 2.3	23	22	32	20
67	68.0	13.3	15.0	2.7	99.0		64	14	21	------
79	52.2	23.9	14.5	4.7	95.3	Hm, 1.0	50	13	32	------
98	54.8	23.9	16.1	.5	95.3	Chlorite, 2.9	52	23	22	------
152	50.6	17.6	27.8	2.6	98.6		53	17	29	------
153	46.7	18.3	8.9	12.1	86.0	Bio, mt, an, 12.0	44	20	12	15
349	16.3	------	1.1	64.5	81.9	Hm, chl, il, an, 17.7	14	------	------	67
387	36.4	9.8	50.0	2.6	98.8		39	15	44	------
388	48.5	15.4	32.8	1.6	98.3		47	22	29	------
392	50.3	24.4	9.5	14.2	98.4		48	38	4	10
562	44.0	9.6	7.2	14.2	75.0	Bio, an, mt, cc, 24.8	40	25	5	15
576	47.5	13.8	1.1	37.2	99.6		49	19	------	30
577	34.1	17.6	22.2	23.1	97.0	cc, mt, 2.9	33	27	17	20
578	36.8	8.1	28.9	24.6	98.4		38	9	26	25
579	47.0	16.8	32.8	1.1	97.7		45	17	37	------
580	36.4	8.1	26.1	27.3	97.9		36	11	25	25
581	59.6	4.8	27.8	6.3	98.5		62	------	32	5
582	32.5	22.5	30.6	8.4	94.0	hm, 3.7	35	31	22	5
583	32.6	20.1	34.5	8.4	95.6	hm, 2.2	33	19	36	7
584	33.9	17.7	28.9	15.2	95.7	hm, 1.6	35	16	29	15
585	32.2	14.4	45.6	6.3	98.5		35	10	46	7
Average	43.1	15.3	21.7	15.5	------		42.8	17.2	21.9	14.2
	Q	M	A	Py	Ka	D	Q	M	A	Py
369 [3]							47	14	------	20
420							45	5	30	10
429							40	15	40	2
464							42	4	42	10
495B							56	18	24	1
Average										

[1] 3(Fe) is a constant used in estimating the total of minerals in excess of quartz, mica, and alkali feldspar in Koipato rocks.

[2] From U.S. Geological Survey rapid rock analyses (U.S.G.S. Bull. 1036–C) by I. H. Barlow, S. D. Botts, W. W. Brannock, G. Chloe, P. L. D. Elmore, M. D. Mack, and H. H. Thomas.

Quartz calculated in this manner agrees with CIPW normative quartz to within one percent in the rocks listed in table 4. The standard deviation of X-ray modal quartz from calculated quartz is 2.2 weight percent (fig. 12), and of albite 3.5 weight percent.[2] The standard deviations of the muscovite and K-feldspar values are large, probably owing chiefly to the apportioning of K_2O and Al_2O_3 in the calculated minerals by means of ideal formulas which are not attained in the natural minerals. Chemical analyses of the rocks that contain andalusite are not amenable to calculation unless a weight concentration for quartz is assumed.

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[2] A regression curve for calculated albite as a function of X-ray modal albite would be the same as that for Na_2O (fig. 17*C*) since the CaO content of the rocks averages less than 0.2 percent, occurring chiefly in traces of calcite.

partial chemical analyses, and oxides calculated from X-ray diffraction modes
altered volcanic rocks of the Koipato Group, Nevada]

X-ray modal minerals—Continued			Partial chemical analyses [2]						Analyses calculated from X-ray modes				Sample
Other	Total Fe	3(Fe)[1]	Total Fe	SiO_2	Al_2O_3	K_2O	Na_2O	Sub-total	SiO_2	Al_2O_3	K_2O	Na_2O	
----------	0.7	2	0.8	77.1	12.6	4.4	3.7	97.8	76.8	13.0	4.3	3.3	----------1
----------	.7	2	.7	77.2	12.4	8.1	.2	97.9	76.1	12.7	8.6	<.5	----------10
----------	.7	2	.6	79.0	12.2	6.1	.1	97.4	78.6	11.9	6.7	<.5	----------46
----------	1.0	3	1.0	78.2	12.4	3.8	1.1	95.5	77.9	13.1	3.3	1.4	----------58
----------	1.0	3	.9	80.7	11.1	3.6	1.4	96.8	78.1	12.7	3.6	1.4	----------58F
----------	1.1	3	.7	75.4	14.6	.2	8.0	98.2	75.5	13.4	<.5	7.7	----------61B
Cc.-------	1.0	3	1.0	66.3	17.9	8.1	2.2	94.5	67.4	18.3	8.0	2.4	----------61W
----------	.3	1	.4	85.2	8.5	4.0	.2	97.9	83.9	9.3	5.2	<.5	----------67
----------	1.6	5	1.1	75.9	12.9	5.3	.6	94.7	76.6	10.9	6.7	<.5	----------79
----------	1.1	3	1.2	77.3	12.7	5.5	.1	95.6	76.5	12.9	6.4	<.5	----------98
----------	.3	1	.4	78.5	12.4	6.8	.3	98.0	79.5	11.9	6.9	<.5	----------152
Bio, 5----	1.3	4	1.7	73.3	13.7	4.5	1.4	92.9	73.3	14.1	5.0	1.8	----------153
Chl------ Mt------- Hm------	6.4	19	6.2	64.3	14.8	.2	7.6	86.9	62.2	14.5	<.5	7.9	----------349
----------	.7	2	.6	75.0	13.4	9.6	.3	98.3	74.2	13.9	9.2	<.5	----------387
----------	.7	2	.9	77.7	11.9	7.3	.2	97.1	75.8	13.8	7.5	<.5	----------388
----------	1.3	4	1.1	77.0	13.3	4.4	1.7	96.4	74.7	17.3	5.2	1.2	----------392
Bio, 10---	1.6	5	1.8	71.1	13.5	3.9	1.7	90.2	69.2	15.9	4.9	1.8	----------562
----------	.7	2	.5	80.0	12.3	1.6	4.4	98.3	78.2	13.2	2.2	3.5	----------576
----------	1.1	3	1.1	72.3	15.2	5.8	2.7	96.0	69.9	17.4	6.1	2.4	----------577
----------	.7	2	.6	76.2	13.2	5.8	2.9	98.1	76.1	13.1	5.5	3.0	----------578
----------	.3	1	.4	77.0	12.9	7.5	.1	97.5	76.6	13.4	8.3	<.5	----------579
----------	1.0	3	.9	75.9	13.4	5.4	3.2	97.9	74.4	13.7	5.5	3.0	----------580
----------	.3	1	.2	84.5	8.4	5.4	.8	99.1	86.1	6.9	5.4	.6	----------581
----------	2.2	7	3.0	68.2	15.5	7.8	1.0	92.5	66.6	16.9	7.4	.6	----------582
----------	1.7	5	2.3	69.8	15.4	8.2	1.0	94.4	69.7	15.3	8.3	.8	----------583
----------	1.7	5	1.7	70.8	14.7	7.0	1.8	94.3	71.3	14.4	6.8	1.8	----------584
----------	.7	2	.6	72.6	15.1	9.4	.8	97.9	74.1	13.7	9.0	.8	----------585
----------	1.18	------	1.2	------	------	------	------	------	------	------	------	------	----Average
Ka	D												
12--------	7	------	------	74.2	21.2	.4	<.1	95.8	74.4	19.7	1.6	<.5	----------369 [3]
----------	10	------	------	66.7	30.3	.6	.1	97.7	68.2	29.2	.6	<.5	----------420
----------	------	------	------	70.5	27.2	.4	<.1	98.1	64.2	32.9	1.7	<.5	----------429
2---------	------	------	------	66.6	31.6	.1	<.1	98.3	66.9	31.6	.5	<.5	----------464
1---------	------	------	------	73.0	22.6	2.3	.2	98.1	74.0	22.8	2.2	<.5	----------495B
----------	------	------	------	74.6	15.3	4.8	1.6	------	74.0	15.7	5.1	1.5	----Average

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[3] Calculated minerals: Samples 369, 420, 429, 464, 495B consist chiefly of SiO_2 and Al_2O_3 in the form of quartz (Q), andalusite (A), muscovite (M), pyrophyllite (Py), kaolinite (Ka), and dumortierite (D); not amenable to calculation.

As the intent of the diffraction analysis of the Koipato rhyolitic rocks was to determine significant compositional differences that would indicate the type, intensity, and pattern of alteration in various parts of the volcanic pile, and in lieu of direct comparison of calculated and X-ray modes, it seems reasonable to compare the chief oxide values calculated from X-ray modes with those of oxides determined chemically. Regression analyses have been made of chemical oxides as a function of calculated oxides, using the 32 sets of oxide values shown in table 4 as well as the 35 sets of alkali oxides of table 5. Regression curves and their corresponding equations for SiO_2, Al_2O_3, K_2O, Na_2O, and difference in alkali oxides are shown in figure 17*A–E*. Minimum differences in the weight percentages of the calculated oxides that are

TABLE 5.—*Chemically determined and calculated alkali oxides from some rhyolitic rocks of the Koipato Group, Nevada*

[Samples were analyzed by I. H. Barlow and P. L. D. Elmore by flame photometer methods described in U.S. Geol. Survey Bulletin 1036–C]

Sample	Chemical		Calculated		Sample	Chemical		Calculated	
	K_2O	Na_2O	K_2O	Na_2O		K_2O	Na_2O	K_2O	Na_2O
114C	7.3	0.64	6.1	0.8	348A	3.4	3.0	3.1	4.1
123	12.6	1.3	11.9	1.2	349A	.11	10.0	.2	11.2
123A	10.8	2.0	9.8	2.0	414	4.6	4.5	4.6	4.5
134B	.16	4.9	.2	4.2	457	11.6	.24	11.9	.2
159D	7.0	.66	5.1	.9	513	4.9	.27	4.8	.2
160	6.8	1.2	5.9	1.4	513A	9.0	1.0	8.3	.8
164M	3.4	.30	2.9	.5	516	5.2	2.8	5.6	2.3
164G	.22	5.3	.2	4.2	529	.16	7.4	.2	7.3
172	4.2	.12	4.7	.2	529A	2.6	6.3	2.6	6.2
220	5.3	1.8	5.6	1.2	529B	8.2	1.2	7.1	1.4
220A	6.4	2.0	7.9	1.2	530	10.5	.24	10.5	.2
221	8.8	.22	10.0	.2	533	5.4	1.2	5.1	1.7
255	8.2	.87	7.5	.7	533A	6.4	2.4	6.2	2.4
255A	.58	6.0	1.3	4.6	548A	5.7	3.7	5.6	3.9
280	3.8	4.4	4.9	4.8	581A	7.0	1.5	5.2	1.8
318	.12	5.8	.2	5.4	601B	.10	5.6	.2	5.6
318A	3.1	2.6	2.9	2.3	661	13.0	.54	11.9	.2
336B	.39	7.6	.2	7.6					

significant at 95 percent confidence over the range of the data are about 2.5 percent SiO_2, 3.5 percent Al_2O_3,[3] 1.6 percent K_2O, 0.8 percent Na_2O, and 1.8 percent difference in alkali oxides. This means that if, for example, two samples differ in X-ray-determined SiO_2 by 2.5 percent or more, one may expect a real difference in their chemical SiO_2 content with about 95 percent confidence. Considering the extreme range in K_2O, Na_2O, and Al_2O_3 in the Koipato rhyolitic rocks, the minimum differences that are significant at 95 percent confidence are generally adequate for allowing detection of significant changes in chemical composition as a function of differences in phase proportions across altered zones.

Calibrated diffraction patterns of three of the samples listed in table 4 are shown in figure 18.

CALIBRATED VERSUS RANDOM PATTERNS

The recording of calibrated diffraction patterns is well worth the slight extra time and effort involved in sample preparation and instrumentation, even if no immediate quantitative use is made of them. They provide permanent records that can be compared directly with calibrated patterns recorded at a later time. Slight relative differences that might not ordinarily be discerned in rocks, especially altered rocks, commonly become apparent by comparing suites of calibrated patterns.

In studying altered mafic volcanic piles, it has been possible to select from calibrated whole-rock patterns, samples that show the

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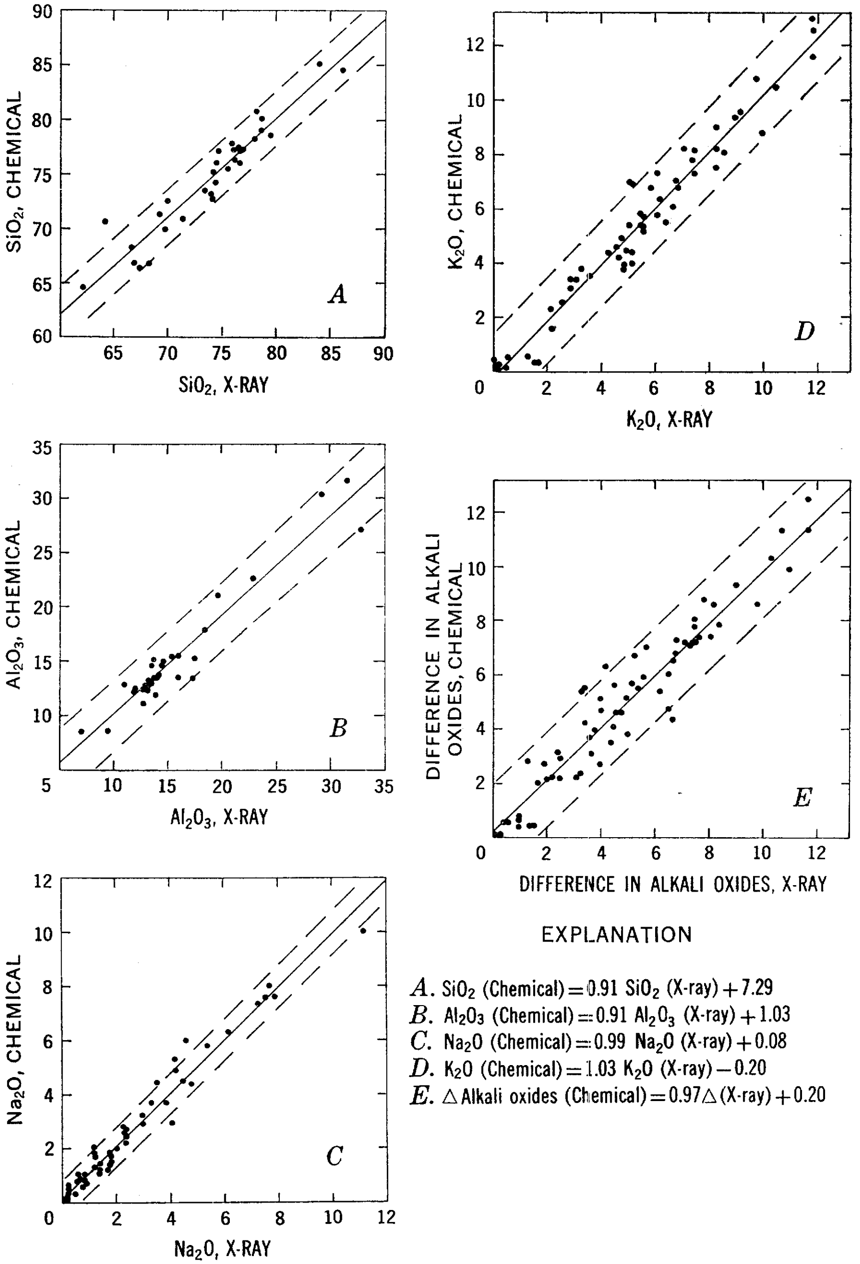
[3] Based on assumed normal bivariate distributions; Al_2O_3 and Na_2O are skewed.



EXPLANATION

A. SiO_2 (Chemical) = 0.91 SiO_2 (X-ray) + 7.29
B. Al_2O_3 (Chemical) = 0.91 Al_2O_3 (X-ray) + 1.03
C. Na_2O (Chemical) = 0.99 Na_2O (X-ray) + 0.08
D. K_2O (Chemical) = 1.03 K_2O (X-ray) − 0.20
E. ΔAlkali oxides (Chemical) = 0.97Δ(X-ray) + 0.20

FIGURE 17.—Regression curves and equations of chemically determined oxides as a function of oxides calculated from X-ray modes (A–D); difference in alkali oxides (*E*). Dashed curves are 95 percent confidence limits. Data from analyses of rhyolitic rocks of the Koipato Group, Nevada (see tables 4 and 5).

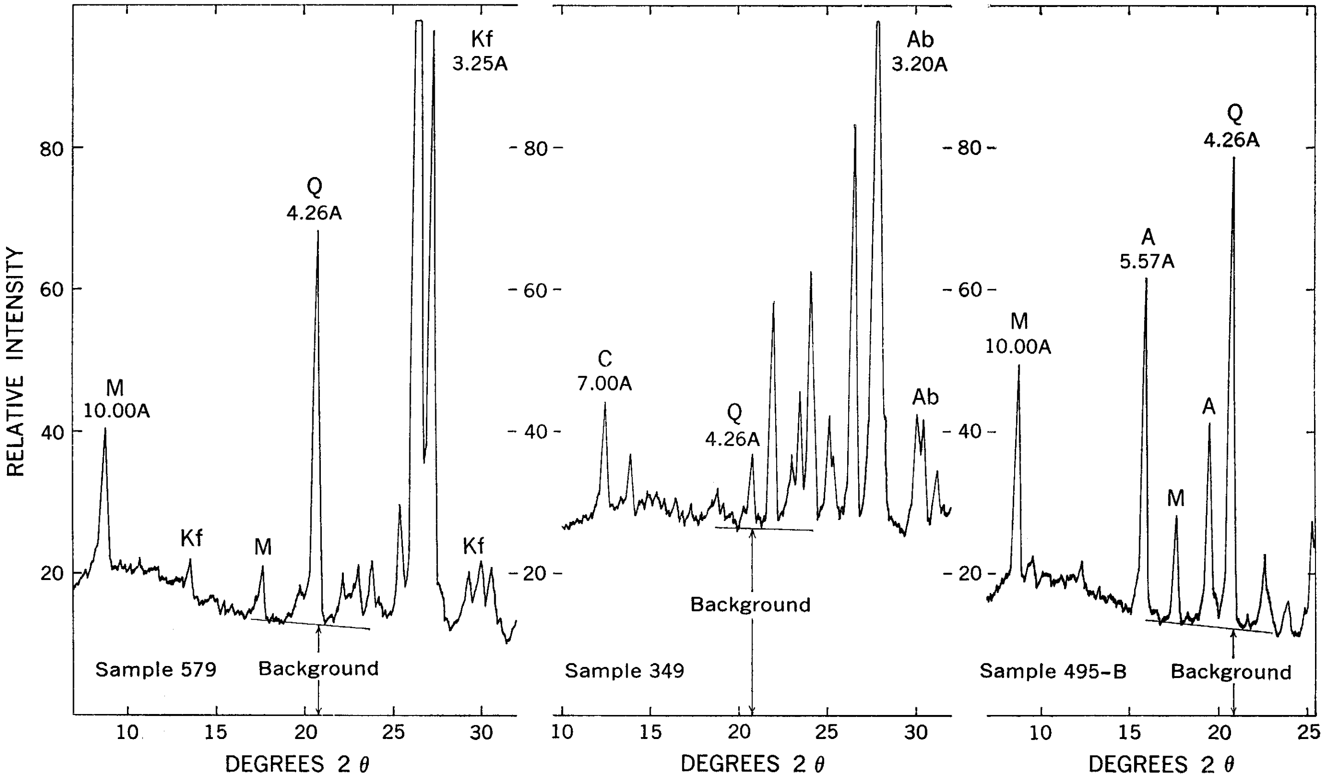


FIGURE 18.—Calibrated diffraction patterns of samples 579, 349, and 495–B, whose partial chemical analyses and X-ray modes are listed in table 4. *A*, andalusite; *Ab*, albite; *C*, chlorite; *Kf*, microcline; *M*, muscovite; *Q*, quartz.

greatest probable differences in phase composition through a given altered zone. Chemical analyses of the selected "end member" samples provide a working range throughout which the chemical composition of intermediate samples can be estimated from calibrated patterns.

Similarly, in working with young salic volcanic rocks ranging from glassy to holocrystalline to hydrothermally altered, the following relative differences in phases are readily apparent from calibrated patterns: (1) Patterns of glassy rocks commonly show only incipient cristobalite or sanidine peaks; (2) holocrystalline varieties may show well-defined quartz lines—with or without a high-temperature silica polymorph—, and commonly two distinct alkali feldspar patterns are developed; (3) in altered types, zeolites, a single low-temperature feldspar, mica and clay minerals, or differences in iron content are readily distinguished.

Any relative differences in calibrated patterns are considerably more meaningful than are differences on randomly recorded patterns.

SAMPLE PREPARATION AND INSTRUMENTATION

SAMPLE PREPARATION

A representative sample aggregating, if possible, 2cc or more, depending on grain size and texture, is chipped from a hand specimen and crushed—not ground—in a hardened steel mortar to pass a 1-mm sieve. The crushing is most easily accomplished in increments—that is, by pouring the fines through the sieve and the remainder back into the mortar and further crushing the remaining coarse material, repeating the crushing and pouring until the entire sample has passed the sieve. The crushed sample is split, preferably with a microsplitter, to about—but not more than—1cc. The crushed split is than ground in a power mortar, such as the Fisher mortar grinder with alumina mortar and pestle and plastic scraper, until the largest particles are less than 40 microns. It has been found in practice that 1 cc of material split from a crushed rock sample that has passed a 1-mm sieve is both representative of the original sample and readily ground to $<$40 microns. A split smaller than 1 cc is apt to be unrepresentative; a larger split requires a correspondingly longer grinding time. For most microcyrstalline silicate rocks about 15 to 30 minutes of grinding is required to reduce 1 cc of crushed ($<$1 mm) sample to less than 40 microns, depending on such variables as the speed of the grinder and the weight of the pestle head. In order to standardize the grinding procedure for a given suite of samples, particle size as a function of grinding time should be checked under the microscope and also on the diffractometer by checking peak-height reproducibility from several different mounts of each of several sample powders.

It must be emphasized that in quantitative diffractometric analysis accuracy is dependent on both reproducibility and maximum peak intensity. Reproducibility is dependent on random orientation of crystallites which is most nearly achieved in sample powders of very fine particle size. Fine particle size also reduces extinction and most microabsorption effects to a negligible level and, hence, allows for near-maximum peak intensity.

PREPARATION OF POWDER MOUNTS

The procedure for mounting the sample powder is essentially that described by McCreery (1949), which minimizes preferred orientation and at the same time produces a plane surface and a powder layer thick enough to allow for maximum diffracted intensities (Klug and Alexander, 1954, p. 252). The sample holder, or cell, is a rectangular sheet of aluminum about 3.5×4×0.16 centimeters with a rectangular hole 1×2 centimeters through the sheet. The sample number is penciled on the side of the cell which will face the X-ray beam, and this side is covered with a clean glass slide held firmly in place with masking tape or a spring-binder paper clip. The cell, with glass slide attached, is placed glass down on a flat surface and an excess of the sample powder is poured into the cavity. The powder is thoroughly tamped with the edge of a small spatula—blade about 1 centimeter wide—so as to fill the cavity evenly and to minimize flowing of the powder along the glass face plate. The powder is then gently compressed with the flat blade of the spatula; a slight surplus, or hump, on the back of the powder cake is preferable to a depression. The back is then covered across the width of the aluminum cell with 1-inch masking tape reinforced on the sticky side with a piece of file card, slightly larger than the cavity, which covers the powder. The backing over the powder cake is pressed firmly, further compressing the powder. The cell is picked up, the glass face plate gently removed, and the masking tape on the back is cut off with scissors flush with the edges of the aluminum holder. Five or six packed cell mounts can be prepared in 15 minutes after a little practice.

The pressure applied in the packing of powder mounts has no significant effect on diffracted intensities (Weiskirchner, 1960; Schmalz, 1958). Also, finely ground powders mounted in a rotating sample holder showed no better reproducibility than those mounted in a stationary holder (Schmalz, 1958). The mounting of sample powders as a slurry on glass slides is not recommended for quantitative work because this method is conducive to preferred orientation and is likely to yield diffracted rays of low intensity owing to inadequate sample thickness.

CALIBRATION AND ANALYTICAL TECHNIQUE

The X-ray source and circuit panel are allowed a warm-up period of about 30 minutes during which time a sample for qualitative analysis may be scanned. During this time, also, the slits and filter are checked. Several powder mounts are prepared. When the instrument has attained equilibrium, the circuit-panel rate meter is zero set and then calibrated so that the recording pen ranges from exactly zero to 60 at 100 cps full-scale deflection on 60 cycles. The desired counting rate and time constant are then set; all settings on the circuit panel remain constant from here on. The recording pen is allowed to run continuously, because turning the chart drive switch on and off occasionally affects the calibration. Only the motor that rotates the goniometer is ever shut off during the course of analyzing several samples.

To calibrate for analysis, the X-ray power source (kilovolt and milliamp dials) is adjusted until both the peak height and background intensities recorded at the 4.26 A quartz line from two or more standard quartz-bearing powder mounts agree consistently with established calibration curves. The standard powder mounts used in the present study contain 30 and 70 percent quartz, and were used in preparing the curve set of figure 9. A final check on calibration is made by measuring background at 4.26 A on a pure magnetite sample. Both peak height and background calibration is assured by following this procedure. Calibration usually requires 10 to 15 minutes after the instrument warm-up period. The calibration should be checked periodically with a standard mount, but in practice, intensity remains remarkably constant.

Scanning of the 4.26 A quartz line from the standard mounts should be always in the same direction and should start at least 1° 2θ ahead of the measured line to assure that full background intensity has been attained.

If a second instrument or a different nickel filter and slit set is used, or if the X-ray beam take-off angle is altered, the intensity-concentration and background curve sets may have to be modified. Slight differences in thickness of nickel filters and width of receiving slits will effect differences in spread between background and peak-height intensity; any significant differences will show up immediately during calibration. Similarly, if a slower scanning speed or time constant is employed, curve sets must be modified, although background will remain the same for any scanning speed or time constant.

For routine analysis of silicate rocks, powders are scanned from 40° to 6° 2θ, as almost all the major minerals in common holocrystalline silicate rocks, both fresh and altered, have prominent measurable reflections in this range. For many felsic rocks, scanning from 32° to 6° is sufficient. The main peaks are rescanned, always in the same direction. The powder mount is then rotated 180°, making essentially a new mount, and the main peaks are again scanned twice in the same direction, beginning at least 1° ahead of the line to be measured. If, from four runs, the mean deviation, especially of the quartz peak, exceeds 0.2 inches, one or more new powder mounts should be prepared. Large deviations in peak heights are usually caused by preferred orientation of crystallites—owing to insufficient grinding and poor mounting—rather than by instrument deficiencies.

In analyzing rhyolitic rocks of the Koipato Group, the chief constituents, as determined from the intensity-concentration curves, invariably totaled from 85 to 105 percent. The total iron,[4] quartz, andalusite, and usually the muscovite determinations were considered absolute; the feldspars were adjusted proportionally so that the total of all constituents was 100 percent.

Analysis of the Koipato rhyolitic rocks, after a standardized routine was established, was accomplished at an average rate of about 40 samples per day by one worker using two diffractometers and four automatic grinders.

STANDARD POWDERS

Standard powders should, if possible, be prepared from constituents contained in the rocks under study. A pure separation of most minerals can be made by centrifuging 20- to 50-micron materials in heavy liquids of appropriate specific gravity. The pure mineral and the selected matrix material are then weighed on 4- by 5-inch glazed paper on an analytical balance in the desired proportions to total 1 to 2 grams. Enough standards should be made, in increments of about 5 percent, to fill the expected range of each constituent in the rocks under study.

To be certain that the pure mineral and the matrix material for each standard powder are thoroughly mixed, the weighed portions are stirred with a small spatula on the glazed paper and then sieved (<1 mm), care being taken to retain all the powder. The stirring and sieving is repeated 3 or 4 times. The mixture is then ground in a power mortar for about 15 minutes to meet the size requirements discussed in the section on sample preparation.

SELECTION OF PEAKS FOR MEASUREMENT

Most of the major minerals in common holocrystalline silicate rocks, both fresh and altered, have prominent reflections in the range 40° to

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[4] The total iron in rocks of the Koipato Group, determined from background intensity, is multiplied by a constant of three for estimating the total of the minor constituents. (See table 4.)

6° 2θ. A few preliminary scans of sample powders from the rocks under study will show which lines are best for measurement.

Quartz.—For quartz, the 4.26 A line (20.8° 2θ), the second strongest quartz line, is best for quantitative determinations, as it is not significantly superposed by peaks of other common rock-forming minerals. Moreover, using copper radiation and 1-degree slits, a standard 20-mm sample mount is almost completely covered by the X-ray beam at the 4.26 A line, affording a better sampling of the powder surface than at higher angles. The only common interference is from the weak 4.25 A K-feldspar line, which, when reflected from finely ground randomly oriented powders, has no significant effect on the 4.26 A quartz line unless the K-feldspar content exceeds about 40 percent, and the quartz content is very low. (See charts by McCreery,1949, reproduced in Klug and Alexander, 1954, p. 303.) There is some evidence, however, that certain low-temperature adularia-type feldspars may reflect a strong peak at 4.25 A. The ratio of the 4.26 A and 1.82 A (50.1° 2θ) quartz lines may be used to check this possible effect.

The 3.34 A quartz line, commonly used in analyzing for quartz in two-component mixtures, is nearly five times as strong as the 4.26 A line and is therefore usually offscale relative to peaks of other minerals when analyzing felsic rocks. Furthermore, the 3.34 A line nearly coincides with strong mica and sillimanite lines and lesser alkali feldspar lines. The 3.34 A line is of use, however, in analyzing unaltered mafic rocks or trachytes in which quartz may occur in low concentrations.

Feldspar.—Plagioclase and K-feldspar are estimated from the composite peaks at about 3.20 A (27.9° 2θ) and 3.25 A (27.4° 2θ), respectively. Owing to compositional variations and to extremely small original crystallite size in some rocks, which reduces intensities, universally reliable determinations of feldspars cannot be made. Furthermore, in scanning from high to low angles, a 3.20 A plagioclase peak will effectively increase the K-feldspar peak at 3.25 A and vice versa. Also, the 3.20 A plagioclase peak must be corrected for slight effects from muscovite.

However, when analyzing a given group of rocks from a common source area, empirically derived correction factors can be applied which allow for reasonably accurate feldspar determinations. Many altered felsic rocks commonly contain only one feldspar (tables 4 and 5) whose concentration can be determined rather accurately. If only K-feldspar is present (fig. 18, sample 579), its "triclinicity" can be determined from the difference between the 131-1$\bar{3}$1 spacings (Goldsmith and Laves, 1954). If only sodic plagioclase is present (fig. 18, sample 349) its anorthite content can be determined from the difference between the 220-$1\bar{3}1$-131 spacings (Smith and Yoder, 1956).

Micas.—At angles smaller than about 18° 2θ, using 1° slits, the primary X-ray beam covers an area larger than the standard 20-mm sample, and intensity measurements from the sample decrease; no interference is encountered from irradiated portions of aluminum sample holders, however. Regardless of intensity loss, mica is generally most reliably measured at the 10.00 A line when only one mica is present in a sample. If a sample contains both biotite and muscovite, the muscovite may be measured, though less reliably, at the 5.00 A line which is about half as strong as the 10.00 A line; biotite has only a very weak peak at 5.00 A. The ratio of the two line intensities allows for an estimation of both biotite and muscovite in the same sample.

Chlorite and kaolinite.—These are measured at the 7.00 A line (12.4° 2θ). If both are present in the same sample, the ratio of the 7.00 A and 4.67 A lines allows for an estimation of each mineral proprovided standards are prepared from chlorite and kaolinite contained in the rocks under study.

Some other common minerals.—Andalusite is reliably measured at 5.57 A (15.9° 2θ); no interference has been encountered at this line. Pyrophyllite is estimated at the 9.25 A line (9.6° 2θ); sillimanite at 5.39 A (16.4° 2θ); amphibole and cordierite at about 8.50 A (10.4° 2θ); and calcite at about 3.03 A (29.4° 2θ).

No attempt has been made in the present study to estimate the weight concentrations of pyroxenes and olivines from diffraction patterns of whole-rock powders. Schmalz (1958), however, has used the 1.63 A line (56.4° 2θ) for determining augite.

CONCLUSION

Calibrated diffraction patterns of whole-rock powders, even when scanned at 2° 2θ per minute, provide a reasonably accurate, rapid, and inexpensive means of determining the weight concentrations of many of the chief silicate minerals and of total iron in fine-grained felsic rocks. The technique is especially well suited to the analysis of altered felsic volcanic rocks. Although the intensity -concentration curves shown, except for quartz and total iron, apply only to rhyolitic rocks of the Koipato Group, the technique can be applied to other fine-grained rocks if appropriate curves are established from artificial powders prepared from minerals contained in the rocks under study. The quartz and iron curves appear to be almost universally applicable. Intensity-concentration and background curve sets can be readily modified for use with direct counting techniques or slower scanning speeds.

Corrections for differences in mass-absorption coefficients between the mineral to be analyzed for and the matrix—sum of all other constituents—are based on differences in the iron content of samples; iron content is measured from background intensity. As the admixing of an internal standard is not required, the rapidity of analysis is considerably increased.

The accuracy of the technique is dependent on the reproducibility of peak heights. Reproducibility is dependent chiefly on random orientation of crystallites in sample powders ground fine enough—less than 40 microns—to reduce extinction and microabsorption effects to a negligible level, thus allowing for maximum intensity of peaks at fixed instrument settings.

The most likely sources of analytical error are: (1) the sample itself, owing chiefly to inadequate grinding and poor mounting of the powders—errors associated with the sample are more serious than those due to the instrument; (2) compositional variations within mineral species; (3) poor calibration of X-ray beam intensity with standard powder mounts; (4) counting rate not properly calibrated initially; zero set is off; (5) slits and filter not centered; and (6) instability of the electronic circuitry.

The success of the technique as applied to altered rhyolitic rocks of the Koipato Group is due to several favorable factors common to many altered volcanic piles: (1) the samples analyzed constitute a large group always containing the same major components, though occurring in a wide range of proportions; (2) all the rocks are holocrystalline; (3) the fine grain of the rocks simplifies sampling from hand specimens and allows for unusually uniform crystallite sizes in finely ground powders; and (4) absorption characteristics are essentially constant for most of the rocks.

Limited experimental work indicates that several other relatively abundant common minerals, including chlorites, amphiboles, and pyrophyllite, can be determined with reasonable accuracy, provided intensity-concentration curves are established from standard powders consisting of minerals separated from the rocks under study.

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