CHEMICAL ANALYSES OF ROCKS WITH THE PETROGRAPHIC MICROSCOPE

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ABSTRACT

The chemical composition of the granite (G-1) was calculated from quantitative mineralogical (modal) analyses of petrographic thin-sections. The percentages of the major constituents, SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O and K_2O were computed. These calculations were compared with the results of wet chemical analyses made by 30 chemists in 25 analytical laboratories. Each constituent calculated from the thin-section analysis of the rock standard lies within the range reported by the chemists. The arithmetic mean of the percentage of each constituent determined by the chemical analyses agrees closely with the analysis calculated from the mode.

A norite sample was also analyzed by petrographic and chemical procedures. Agreement between the two techniques for this sample was close.

This study indicates that for rocks in which the composition of the individual minerals has been obtained by optical measurements, the major constituents can be determined with the petrographic microscope by modal analyses, and the results may be considered reliable.

INTRODUCTION

Chemical analyses of rocks have been reported in the geological literature for nearly one hundred years. They are expensive and time-consuming to make, yet are essential for many types of investigation.

Calculation of the chemical composition from the mineral distribution (mode), as determined under the petrographic microscope, is not commonly reported in present-day geological literature. Delesse suggested as long ago as 1886 that the chemical composition can be determined from a modal analysis of the rock. Glagolev (1933) introduced the point-counting procedure, recently renovated by Chayes (1949), and advocated the calculation of the chemical composition of rocks from the results of modal studies. Whitten (1953) calculated the chemical composition of granite and quartzite from their modes and considered this method (p. 337) "a technique for roughly evaluating the chemical variability within a suite of rocks." Balasanyan (1957), using the techniques of Kuznetsov (1947) and Niggli (1936), determined the mode of the rock and expressed the chemical composition in terms of moles of the major minerals present. Balasanyan reported that instead of expensive, time-consuming chemical analyses, precise modal analyses can be used to give results comparable to detailed wet chemical analyses. However, this type of approach does not permit comparison of the rock under investigation with the wealth of chemical analyses available in the literature. Wahlstrom (1950, p. 237) refers to the calculation of chemical composi-

tion from the mode but notes "it cannot be assumed that the computed chemical composition of the rock is very accurate."

A recent survey by Fairbairn and others (1951) investigated the precision and accuracy in chemical and modal analyses of rocks. Two rocks, a granite designated G-1 and a diabase designated W-1, were analyzed by conventional chemical procedures in 25 reputable analytical laboratories throughout the world. These same rocks were subjected to modal analyses at the Geophysical Laboratory (Chayes 1951) and at the Massachusetts Institute of Technology (Chayes 1952). Comparisons were made between the actual mineral distribution (mode) of these rocks and the computed mineral distribution (norm), and attempts were made to explain the discrepancy between the two. The chemical composition of these rocks was not calculated from the modal analyses, and therefore no comparison was made between the results of standard chemical procedure and the chemical composition derived from thin-section petrography. A comparison would be interesting to see how the accuracy of an analysis computed from data obtained with a petrographic microscope compares with the chemical determinations. Modal analyses do not require expensive equipment normally unavailable in the petrographic laboratory, and one thin-section analysis can be made in less than an hour.

If agreement between the two techniques can be demonstrated to be close, the petrologist can extend the petrographic method of chemical analysis to many research problems. The purpose of this note is to compare the results of the two methods of analysis for one of the two rocks* and to apply the two techniques to an "unknown" rock sample. On the basis of these comparisons it can be decided whether calculation of the chemistry of the rocks from examination with the petrographic microscope can be considered reliable and adequate for petrological investigations.

The work of Fairbairn, et al. (op. cit.), revealed serious discrepancies in many of the chemical analyses made on the two rocks. The wide range of results for individual oxides reported by the chemists came as a surprise and shock to many petrologists. However Fairbairn notes (p. 69) that . . . "the likelihood of occurrences of many of these discrepancies is of course commonplace to chemists and causes no surprise if the conditions of analysis are appreciated." He continues (p. 70), "ranges reported in the granite and diabase standards are greater than the compositional limits for related but distinctly different rock types," whereas (p. 5) "precision obtained by modal analyses proved superior to that shown by norms calculated from the individual chemical analyses."

* The rock studied is the granite G-1. Since the optics and composition of the feldspar and pyroxene in the diabase W-1 are not available from the literature, calculation of the chemical composition from mineralogical data cannot be made satisfactorily for this rock.

PROCEDURE

Comparisons between the chemically and optically determined composition of a granite and a norite were made. The chemical composition of the granite G-1 was calculated from modal analysis made by Chayes (1951, p. 61) and represents the mean of measurements on sixteen thin sections. The results were then compared with the wet chemical analyses presented by Schlecht and Stevens (1951) (Table 1).

TABLE 1. CHEMICAL COMPOSITION OF GRANITE G-1 AS DETERMINED BY ROUTINE
CHEMICAL AND PETROGRAPHIC PROCEDURES

	I	II	III	IV	V
	Range of Chemical Analyses Reported by 30 Chemists*	Arithmetic Mean of Rock Analyses†	Chemical Analysis from Mode for Comparison with I and II‡	Arithmetic Mean of Rock Analyses Recalculated to 100%	Chemical Analysis From Mode§
SiO_2	71.0–72.7%	72.2%	71.1%	72.9%	71.7%
Al_2O_3	13.2–16.0	14.4	14.7	14.6	14.9
MgO	0.2– 0.8	0.4	0.5	0.4	0.5
FeO	0.8– 1.4	1.0	1.3	1.0	1.3
Fe_2O_3	0.3– 1.7	0.9	1.0	0.9	1.0
CaO	1.2– 1.9	1.4	1.5	1.4	1.5
Na_2O	2.6– 4.0	3.3	2.8	3.3	2.8
K_2O	3.9– 6.9	5.5	6.3	5.5	6.4
		99.1%	99.2%	100.0%	100.1%

* Dennen, Ahrens, and Fairbairn, 1951, p. 33–34, Figs. 1 and 2. (TiO_2, MnO, P_2O_5, and H_2O omitted; not recalculated to 100 per cent.)

† Dennen, Ahrens, and Fairbairn, 1951, p. 37, Table 14. (TiO_2, MnO, P_2O_5, and H_2O omitted; not recalculated to 100 per cent.)

‡ As TiO_2, MnO, P_2O_5, and H_2O have been omitted from the chemical analyses listed in Columns I and II, the chemical analysis calculated from the mode (Column V) has been recomputed for direct comparison with Columns I and II.

§ Calculation by the writer from modal analyses of Chayes (1951, p. 61).

A specimen of norite from the Caribou Lake intrusion, Canada (Friedman, 1957) was analyzed in thin section by the writer. The chemical composition of the rock was computed from the mode, and the results were compared with chemical analyses of the same rock made by the Rock Analysis Laboratory of the University of Minnesota. The results are compared in Table 2.

Analysis by petrographic procedure involves three steps: 1. Identification of the minerals present and assigning each a formula based on optical

data; 2. A determination of the relative abundance of each mineral using counting techniques; 3. Computation of the weight per cent chemical composition. The first two steps are routine and are discussed elsewhere (Tröger 1952, Chayes 1949).

The third step of calculating the chemical composition from the modal analysis involves the conversion of the mode to weight per cent. The weight per cent of the minerals present in the granite, except for potas-

TABLE 2. CHEMICAL COMPOSITION OF NORITE AS DETERMINED BY ROUTINE CHEMICAL AND PETROGRAPHIC PROCEDURES

	Chemical Composition Determined by Chemical Analysis*	Chemical Composition Calculated from Mode
SiO_2	51.8%	52.7%
Al_2O_3	19.8%	18.4%
Fe_2O_3	1.1%	1.1%
FeO	6.2%	6.6%
MgO+CaO†	18.3%	18.6%
[MgO]	[8.9%]	[10.6%]
[CaO]	[9.4%]	[8.0%]
Na_2O	2.5%	2.5%
K_2O	0.3%	0.1%
Total	100.0%	100.0%
	Analyst Doris Thaemlitz	Gerald M. Friedman

* Recalculated to 100 per cent, omitting H_2O, CO_2, TiO_2, P_2O_5, MnO, S, and Cl.

† A probable error in the identification of some pyroxene grains brought about a small discrepancy between chemical and petrographic analyses for CaO and MgO. The sums of CaO and MgO for the two techniques agree as shown in this table.

sium feldspar and plagioclase, was taken from Dennen, Ahrens, and Fairbairn (1951, p. 42). Specific gravity data given by Tröger (1952) were used to convert the modal values of the feldspars to weight per cent. In the norite sample the specific gravities of plagioclase, pyroxene, and biotite present were determined from tables of Tröger (1952). The specific gravities of quartz and magnetite were taken from Dana and Ford (1932). The specific gravity of the garnet in norite was determined for the writer by D. K. Smith.

For the granite calculation the potassium feldspar was considered a pure orthoclase or microcline without Na_2O substitution. For plagioclase a value of An_{23} has been obtained from physical parameters (Chayes

1952, p. 213). The theoretical composition given by Dana and Ford (1932) was used for muscovite and magnetite. The gamma index of biotite ($\gamma = 1.637 \pm 0.005$) was experimentally determined and the biotite composition was approximated with the aid of a table by Winchell and Winchell (1951, p. 374).

Chayes (1951, p. 60–61) distinguishes between opaque and non-opaque accessory minerals. The non-opaque accessories have not been identified, but in some calculations (cf. Dennen, Ahrens, and Fairbairn, 1951, p. 42) both types of accessories have been lumped as magnetite, a procedure which has been adopted in the present study.

For the norite the composition of plagioclase, pyroxene, and garnet were determined from optical parameters with the aid of tables (Crump and Ketner 1953, p. 31; Hess, 1952, p. 180, Fig. 2; Walker and Poldervaart, 1949, p. 631; Tröger, 1952, p. 12). The detailed petrography and mineralogy of this rock are described elsewhere (Friedman, 1957, p. 1544–1545). For biotite an average chemical composition given by Wahlstrom (1950, p. 238) was used. The exact composition of amphiboles cannot be obtained from optical parameters, and an average composition given by Wahlstrom (1950, p. 238) was used.

RESULTS AND DISCUSSION

Column I in Table 1 presents the range of values for the oxides determined in the granite G-1 by the chemists (Dennen, Ahrens, and Fairbairn, p. 33–34). Columns II and IV show the arithmetic mean of these analyses (Dennen, Ahrens, and Fairbairn, p. 37), and Columns III and V the chemical composition computed from the modal analysis of Chayes (1951). The calculations for arriving at the chemical composition from the mode are given in the Appendix.

TiO_2, MnO, H_2O, and P_2O_5 which have been determined chemically for the granite have not been obtained by calculation from the mode.

The most outstanding observation from this comparison is that each constituent computed from the mode for the granite lies within the range reported from chemical analyses. Moreover, comparison of Columns IV and V of Table 1 shows good agreements between the arithmetic mean of the chemical analyses and the calculated composition from the mode. Schlecht and Stevens (1951, p. 7) point out that assignment of "correct" values for the composition of the rock is not justified on the basis of chemical analyses. Therefore in the absence of knowledge of the "true" composition of this rock, no precise appraisal can be made of the error involved in determining the chemical composition from modal studies. However the discrepancy between chemical and petrographic procedures appears to be small enough to justify wider application of the petrographic technique to petrological and geochemical studies of rocks.

The granite G-1 contains minerals which are easily identified and for which modal analyses are relatively simple to make. To test the usefulness of the petrographic method further, a norite sample was selected in which reaction rims, cataclastic deformation, and replacement by secondary minerals make modal studies more difficult. This rock has been described in detail elsewhere (Friedman, 1957, p. 1540–1541). For the mode of the norite and the composition and specific gravity of the norite minerals refer to the appendix. Table 2 shows that the discrepancy between the results of chemical and petrographic procedures is remarkably small for six of the eight constituents. The only disparity is for CaO and MgO. However, the sum of CaO and MgO agrees closely for the two analyses. The error in these two constituents is probably a result of misidentifying some clinopyroxene grains as orthopyroxene. Even so, the discrepancy between the two analyses for CaO and MgO is not serious if the wide range of results for MgO and CaO in the diabase W-1, as reported by the chemists, is considered. Considering the complexity of the rock, agreement between the two techniques is considered highly satisfactory. Analysis of the norite sample shows that the chemical composition of mineralogically and texturally complex rocks can be determined satisfactorily with the petrographic microscope.

This study indicates that for rocks in which the composition of the individual minerals can be obtained by optical measurements, the major constituents can be determined with the petrographic microscope and the results can be considered reliable for most purposes. Petrologists should therefore make more chemical analyses with the aid of the microscope. Glasses, shales, and fine-grained rocks are not amenable to determination of chemical composition by the microscopic technique.

The major uncertainty of calculations of the kind presented in this paper is the assignment of a specific chemical composition to complex minerals, such as amphiboles, for which satisfactory correlations between optical properties and chemical composition are not available. This may be serious if these minerals make up a major part of the rock.

Conclusions

From this study it is concluded that

1. Each constituent computed from the mode for the granite G-1 lies within the range reported by the chemists. The arithmetic means of the chemical analyses agree closely with the analyses calculated from the mode.

2. Analysis of the norite sample shows that the chemical composition of mineralogically and texturally complex rocks can be determined satisfactorily with the petrographic microscope.

3. This study indicates that for rocks in which the composition of the

individual minerals can be obtained by optical measurements, the major constituents can be determined with the petrographic microscope, and the results can be considered reliable for most purposes.

4. Petrologists should make more chemical analyses with the petrographic microscope.

APPENDIX

I. CALCULATION OF CHEMICAL COMPOSITION OF GRANITE, G-1, FROM MODE

Mineral	Mode (Chayes, 1951 p. 61)	Weight % (Dennen, Ahrrens, and Fairbairn p. 42)	Sp.G	Weight %	Weight % recalculated to 100%, or grams in 100 g. of rock
Quartz	27.5%	28.0%		28.0%	27.9%
Potassium Feldspar	35.4⎰		2.57	34.5	34.4
Plagioclase An$_{23}$	31.4⎱	65.9	2.63	31.4	31.2
Muscovite	1.3	1.4		1.4	1.4
Biotite	3.2	3.6		3.6	3.6
Magnetite	1.2	1.5		1.5	1.5
		100.4%		100.4%	100.0%

Quartz SiO_2 27.9 g. SiO_2 in 100 g. of rock.
Potassium feldspar $KAlSi_3O_8$ 34.4 g. in 100 g. of rock.

	Mol. wt.	%	
$\frac{1}{2}$ K_2O	47.1	16.9×34.4 g.=	5.8 g. K_2O
$\frac{1}{2}$ Al_2O_3	51.0	18.3×34.4 g.=	6.3 g. Al_2O_3
3 SiO_2	180.3	64.8×34.4 g.=	22.3 g. SiO_2
	278.4	100.0	34.4 g.

Plagioclase $Ab_{77}An_{23}$ 31.2 g. in 100 g. of rock.

$NaAlSi_3O_8$	Mol. wt.	$CaAl_2Si_2O_8$	Mol. wt.	Ab.
$\frac{1}{2}$ Na_2O	31.0	CaO	56.1	0.77×262.3=202.0
$\frac{1}{2}$ Al_2O_3	51.0	Al_2O_3	102.0	An.
3 SiO_2	180.3	2 SiO_2	120.2	0.23×278.3= 64.0
	262.3		278.3	Mol. wt. $Ab_{77}An_{33}$=266.0

$$\left(\frac{0.77\times31.0}{266.0}\right)\times100= \ 9.0\%=2.8 \text{ g. } Na_2O$$

$$\left(\frac{0.23\times56.1}{266.0}\right)\times100= \ 4.9\%=1.5 \text{ g. CaO}$$

$$\left(\frac{0.77\times(51.0)+0.23(102.0)}{266.0}\right)100= \ 23.6\% = \ 7.4 \text{ g. } Al_2O_3$$

$$\left(\frac{0.77(180.3)+0.23(120.0)}{266.0}\right)100= \ 62.6\% = 19.5 \text{ g. } SiO_2$$

$$100.1\% \quad 31.2 \text{ g.}$$

Muscovite   1.4 g. in 100 g. of rock.

Composition by Dana and Ford (1932)		Composition H_2O-free basis	
SiO_2	45.2%	47.3%×1.4 g. = 0.7 g. SiO_2	
Al_2O_3	38.5	40.3	= 0.6 g. Al_2O_3
K_2O	11.8	12.4	= 0.2 g. K_2O
H_2O	4.5		
	100.0	100.0	1.5 g.

Biotite   3.6 g. in 100 g. of rock.

25% Phlogopite	$K_2Mg_6(OH)_4Si_6Al_2O_{20}$
25% Eastonite	$K_2Mg_5Al(OH)_4Si_5Al_3O_{20}$
25% Siderophyllite	$K_2Fe_5Al(OH)_4Si_5Al_3O_{20}$
25% Annite	$K_2Fe_6(OH)_4Si_6Al_2O_{20}$

Phlogopite	Eastonite	Siderophyllite	Annite
K_2O = 94.2	K_2O = 94.2	K_2O = 94.20	K_2O = 94.2
$6MgO$ = 242.0	$5MgO$ = 201.6	$5FeO$ = 359.25	$6FeO$ = 431.1
Al_2O_3 = 102.0	$2Al_2O_3$ = 203.9	$2Al_2O_3$ = 203.92	Al_2O_3 = 102.0
$6SiO_2$ = 360.5	$5SiO_2$ = 300.5	$5SiO_2$ = 300.45	$6SiO_2$ = 360.2
$2H_2O$ = 36.0	$2H_2O$ = 36.0	$2H_2O$ = 36.00	$2H_2O$ = 36.0
834.7	836.2	993.82	1023.8

$$0.25(834.7)+0.25(836.2)+0.25(993.8)+0.25(1023.8)=922.1=\text{M.W. of biotite}$$

$$\frac{94.2}{922.1}\times100=10.21\% \ K_2O$$

$$\frac{0.25(242.0)+0.25(201.6)}{922.1}\times100=12.03\% \ MgO$$

$$\frac{0.25(359.25)+0.25(431.1)}{922.1}\times100=21.43\% \ FeO$$

$$\frac{0.25(102.0)+0.25(203.9)+0.25(203.9)+0.25(102.0)}{922.1}\times100=16.59\% \ Al_2O_3$$

$$\frac{0.25(360.5)+0.25(300.5)+0.25(300.5)+0.25(360.5)}{922.1}\times100=35.84\% \ SiO_2$$

$$\frac{36.0}{922.1}\times100=\frac{3.90\%}{100.0\%} \ H_2O$$

Recalculated on H_2O-
free basis

K_2O	10.6%×3.6 g. = 0.382 g. K_2O
MgO	12.5	= 0.450 g. MgO
FeO	22.3	= 0.803 g. FeO
Al_2O_3	17.3	= 0.623 g. Al_2O_3
SiO_2	37.3	= 1.343 g. SiO_2
	100.0	3.601 g.

Magnetite 1.5 g. in 100 g. of rock.

Mol. wt.

FeO	71.8	$\frac{71.8}{231.4} \times 100 = 31.0\% = 0.5$ g.
Fe_2O_3	159.5	$\frac{159.6}{231.4} \times 100 = 69.0\% = 1.0$ g.
	231.4	1.5 g.

Chemical Analysis (Petrographic Method)

SiO_2	71.7%
Al_2O_3	14.9
Fe_2O_3	1.0
FeO	1.3
MgO	0.5
CaO	1.5
Na_2O	2.8
K_2O	6.4
	100.1%

II. MODE OF NORITE, AND SPECIFIC GRAVITY OF MINERALS IN NORITE

Mineral	Mode	Sp.G.
Plagioclase	63.2%	2.70
An_{62}		
Clinopyroxene	1.0	3.34
En_{47} Fs_{13} Wo_{40}		
Orthopyroxene	28.7	3.39
Of_{23}		
Hornblende	4.8	3.20
Biotite	1.1	3.00
Garnet	1.0	3.84
Andradite 21%		
Pyrope 47%		
Almandine 32%		
Magnetite	0.1	5.20
Quartz	0.1	2.65
	100.0%	

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