

NOTES AND NEWS

ESTIMATION OF CHEMICAL COMPOSITION OF ROCKS

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Recently Friedman (1960) demonstrated how the chemical composition of rocks could be calculated from the mineralogical mode determined optically. The constituents which are fairly accurately computed are SiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MgO , CaO , Na_2O and K_2O . Each of these constituents calculated from the thin section analyses of the standard granite, G-1 (Fairbairn *et al.*, 1951), lies within the range reported by the chemists, and except for the alkalies, the computed concentrations of the elements are close to the arithmetic mean of G-1 rock analyses. Friedman (1960) also computed the chemical composition of a norite and obtained fair agreement with the chemical analysis of the same rock.

As calculation of chemical composition from the mineralogical mode and vice versa is, and has been, of great concern to petrologists some additional remarks seem appropriate. It is probably stating the obvious to say that the accuracy of these calculations depends upon at least two conditions:

- (1) The mineral percentages computed from thin sections must be reliable.
- (2) The optically determined composition of the minerals must be accurate.

If these two conditions are ideally satisfied, the chemical composition can be calculated with great accuracy. Rocks which for any reason, *e.g.*, grain size, secondary alteration, etc., do not allow these conditions to be satisfied are not amenable to this kind of treatment.

In general, granitic, or quartzo-feldspathic rocks show better agreement between analysed and calculated composition than rocks rich in ferro-magnesian minerals. This is because of the uncertainty and difficulty in deriving the exact chemical composition of ferro-magnesian minerals by optical means alone.

Friedman (1960) computed the chemical composition as weight per cent of the oxides. This demands a knowledge of the specific gravity of the minerals and the weight percentage of the various components in the pure mineral phases. There seems to be no reason why weight percentages of the elements must be used, inasmuch as unnecessary uncertainties and rather cumbersome calculations are introduced. The presence of elements in minerals and rocks is controlled by other factors than weight.

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Of more direct use to the petrologist is the calculation of "equivalent molecular units" (Niggli, 1936), or even better, calculation of cation per cent. (For an explanation of this calculation, see Barth, 1952, pp. 76-82.)

Chemical analyses of G-1 and norite discussed by Friedman (1960) are calculated into cation per cent in Tables 1 and 2 respectively (columns I-IV).

Calculation of cation per cent of elements from mineral formulae is simple. Potassium feldspar KAlSi_3O_8 consists of 1 $\text{KO}_{1/2}$ +1 $\text{AlO}_{1/2}$ +3 SiO_2 , together 5 units. 100% potassium feldspar contains 20 cat. %

TABLE 1. G-1—GRANITE

	I	II	III	IV	V
SiO_2	72.9	60	1214.0	68.1	68.2
$\text{AlO}_{1/2}$	14.6	51	286.3	16.0	15.7
$\text{FeO}_{1/2}$	0.9	80	11.3	0.6	0.8
FeO	1.0	72	13.9	0.8	
MgO	0.4	40	10.0	0.6	
MgO+FeO	1.4			1.4	1.4
CaO	1.4	56	25.0	1.4	1.4
$\text{NaO}_{1/2}$	3.3	31	106.4	6.0	4.9
$\text{KO}_{1/2}$	5.5	47	117.0	6.5	7.6
$\text{NaO}_{1/2}$ + $\text{KO}_{1/2}$				12.5	12.5
			1783.9		

- I. Arithmetic mean of rock analyses, weight per cent. Calculated to 100%.
- II. Equivalent molecular weight.
- III. Cation proportions $\times 1000$.
- IV. Cation per cent from chemical analyses.
- V. Cation per cent calculated from mineralogical mode using standard mineral formulae of Table 3.

$\text{KO}_{1/2}$, 20 cat. % $\text{AlO}_{1/2}$, 60 cat. % SiO_2 . Muscovite $\text{KA}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ consists of 1 $\text{KO}_{1/2}$ +3 $\text{AlO}_{1/2}$ +3 SiO_2 +2 ($\text{HO}_{1/2}$), together 9 units, and 100% muscovite contains 100/9 cat. % $\text{KO}_{1/2}$, 3.100/9 cat. % $\text{AlO}_{1/2}$, 3.100/9 SiO_2 , 2.100/9 $\text{HO}_{1/2}$.

The mineral content determined microscopically represents volume percentages. It can be shown that for common rocks the cation percentages calculated in this way from the volume of the minerals approximate the actual cation percentages of the total rock.

Table 3 lists the standard formulae of the modal minerals in G-1 and norite discussed by Friedman (1960). (With more detailed optical data for the minerals in the two rocks it is possible to express the mineral com-

TABLE 2. NORITE

	I	II	III	IV	V
SiO ₂	51.8	60	863.2	47.2	47.8
AlO _{1 1/2}	19.8	51	388.3	21.2	22.1
FeO _{1 1/2}	1.1	80	13.8	0.75	0.2
FeO	6.2	72	86.1	4.7	
MgO	8.9	40	222.5	12.2	
MgO+FeO				16.9	16.2
CaO	9.4	56	167.8	9.2	8.8
NaO _{1/2}	2.5	31	80.6	4.4	4.8
KO _{1/2}	0.3	47	6.4	0.35	0.1
NaO _{1/2} +KO _{1/2}				4.75	4.9
			1828.7		

I. Weight per cent of rock analysis calculated to 100%.

II. Equivalent molecular weight.

III. Cation proportions $\times 1000$.

IV. Cation per cent from chemical analysis.

V. Cation per cent calculated from mineralogical mode using standard mineral formulae of Table 3.

positions more exactly than in Table 3, but the standard formulae are close enough for the present considerations.)

In Tables 4 and 5 are the mineral modes of G-1 and norite respectively calculated into cation per cent. As water is not considered, the sum of the remaining constituents is recalculated to 100. These may be compared with the cation percentages calculated from the chemical analyses and for ease of comparison are set down as column V in Tables 1 and 2.

Comparisons between columns IV and V in Tables 1 and 2 show the same similarity between computed and analytically determined cation percentages as shown by Friedman (1960) for the weight percentages. In the first case no attempt was made to distinguish between MgO and FeO in the minerals. However, it is seen that the sum of these two elements is obtained with great accuracy. This is an advantage of calculat-

TABLE 3. STANDARD FORMULAE OF MINERALS

Quartz: SiO ₂	Hornblende: Ca ₂ (Mg, Fe) ₃ Al ₂ Si ₆ Al ₂ O ₂₂ (OH) ₂
Potassium feldspar: KAlSi ₃ O ₈	Biotite: K(Mg, Fe) ₃ AlSi ₃ O ₁₀ (OH) ₂
Albite: NaAlSi ₃ O ₈	Muscovite: KAl ₂ AlSi ₃ O ₁₀ (OH) ₂
Anorthite: CaAl ₂ Si ₂ O ₈	Garnet: Ca ₃ (Mg, Fe) ₆ Al ₄ Fe ₂ (SiO ₄) ₉
Orthopyroxene: (Mg, Fe)SiO ₃	Magnetite: FeOFe ₂ O ₃
Clinopyroxene: Ca(Mg, Fe)Si ₂ O ₆	

TABLE 4. CALCULATION OF CATION PER CENT OF THE ELEMENTS FROM THE MINERALOGICAL MODE OF G-1

	Mode Volume per cent	SiO ₂	KO ₂	NaO ₂	AlO ₂	FeO ₂	CaO	MgO+FeO
Quartz	27.5	27.50						
K-feldspar (Plag. An ₂₈)	35.4 31.4)	21.24	7.08		7.08			
Albite	24.2	14.52		4.84	4.84			
Anorthite	7.2	2.88			2.88		1.44	
Muscovite	1.3	0.44	0.14		0.44			
Biotite	3.2	0.96	0.32		0.32			0.96
Magnetite	1.2					0.8		0.4
		67.54	7.54	4.84	15.56	0.8	1.44	1.36
Recalculated to 100%		68.2	7.6	4.9	15.7	0.8	1.4	1.4

ing the mineral mode into cation per cent; a direct calculation of the mode into weight per cent demands a knowledge of the MgO/FeO ratio in the minerals, for the atomic weights of the two elements differ.

Similarly the cation per cent sum of the alkalis is obtained with great

TABLE 5. CALCULATION OF CATION PER CENT OF THE ELEMENTS FROM THE MINERALOGICAL MODE OF NORITE

	Mode Volume per cent	SiO ₂	KO ₂	NaO ₂	AlO ₂	CaO	FeO ₂	MgO+FeO
Quartz (Plag. An ₆₂)	0.1 63.2)	0.10						
Albite	24.0	14.40		4.80	4.80			
Anorthite	39.2	15.68			15.68		7.84	
Orthopy- roxene	28.7	14.35						14.35
Clinopy- roxene	1.0	0.50					0.25	0.25
Hornblende	4.8	1.68			1.12		0.56	0.84
Biotite	1.1	0.33	0.11		0.11			0.33
Garnet	1.0	0.37			0.17	0.08	0.12	0.25
Magnetite	0.1					0.07		0.03
		47.41	0.11	4.80	21.88	0.15	8.77	16.05
Recalculated to 100%		47.8	0.1	4.8	22.1	0.2	8.8	16.2

accuracy. The difference between computed and analysed cation per cent of sodium and potassium in G-1 is explained by the fact that all of the modal potassium feldspar was calculated as KAlSi_3O_8 , thereby neglecting that a substantial amount of $\text{NaAlSi}_3\text{O}_8$ enters the same phase (as perthites). The ratio between KAlSi_3O_8 and $\text{NaAlSi}_3\text{O}_8$ in perthites cannot be determined optically. The failure to do so will not affect the sum of the cation percentages but will grossly affect the weight per cent calculations.

The computed concentration of ferric iron in the norite is seen to be unreliable. Though the analytical determination of ferric iron seems to be distinctly inferior to those of other constituents at the same concentrations (Ahrens, 1957), the reason for the great difference between computed and analytically determined cation per cent ferric iron in the norite is due to the fact that ferric iron is not included in the standard formulae of the ferro-magnesian minerals in Table 3. In these minerals ferric iron substitutes for Al in 6-coordination, and it should be noted that the computed cation per cent Al in the norite is higher than that determined analytically.

As the FeO , MgO , $\text{NaO}_{1/2}$, $\text{KO}_{1/2}$ concentrations and the FeO/MgO and $\text{NaO}_{1/2}/\text{KO}_{1/2}$ ratios are of special value in petrological considerations, the difficulty in determining them optically is a serious deficiency. However, we need not consider optical methods alone and it will be shown how a combination of modal analyses with very simple analytical techniques may be applied.

A flame photometer for alkali determinations will soon be just as common in geological institutions as the polarizing microscope, and it can be used by everyone. Consider now the G-1 example. Based on thin section analyses the cation percentages listed in column V, Table 1 are obtained. Flame photometric alkali determinations give the concentrations of sodium and potassium listed in column I. As the sum of the cation percentages of $\text{NaO}_{1/2}$ and $\text{KO}_{1/2}$ may be computed accurately (compare columns IV and V) the cation per cent of $\text{NaO}_{1/2}$ and $\text{KO}_{1/2}$ may be found by the following relation:

$$\left(\frac{\text{wt. } \% \text{ Na}_2\text{O}}{\text{mol. wt. NaO}_{\frac{1}{2}}} + \frac{\text{wt. } \% \text{ K}_2\text{O}}{\text{mol. wt. KO}_{\frac{1}{2}}} \right) \cdot X = \text{sum of cat. } \% \text{ NaO}_{\frac{1}{2}} + \text{KO}_{\frac{1}{2}} \quad 1.$$

$$\left(\frac{3.3}{31} + \frac{5.5}{47} \right) \cdot X = 12.5$$

$$X = 56$$

$$\text{cation per cent NaO}_{\frac{1}{2}} = \frac{3.3}{31} \cdot 56 = 6.0$$

$$\text{cation per cent KO}_{\frac{1}{2}} = \frac{5.5}{47} \cdot 56 = 6.5$$

(The factor X is the same as the conversion factor used in recalculating the cation proportions (column III) into cation per cent (column IV), or rather 1000 times this factor, *i.e.*,

$$X = \frac{100}{1783.9} \cdot 1000.)$$

In case of the norite X also equals 56, and the cation percentages are: $\text{NaO}_{1/2}$ 4.5, and $\text{KO}_{1/2}$ 0.4.

Similarly, the determination of ferrous iron by titration demands very little laboratory equipment and is done in one single determination on the bulk rock. Again, in the case of G-1, having determined the weight per cent of FeO as 1.0% (Table 1, column I), the cation per cent of FeO is found by the relation:

$$\frac{\text{wt. \% FeO}}{\text{mol. wt. FeO}} \cdot X = Y \quad 2.$$

X is the same factor as in equation 1, *i.e.*, 56, and Y is the cation per cent of FeO.

$$\frac{1.0}{72} \cdot 56 = Y$$

$$Y = 0.8 = \text{cation per cent FeO.}$$

$$\text{cation per cent MgO} = 1.4 - 0.8 = 0.6.$$

In case of the norite the cation per cent of FeO is found to be 4.8, and of MgO 11.4.

Having obtained the cation percentages of the elements through the combination of optical and chemical methods the weight per cent is, if for some reason this quantity should be desired, easily obtained by multiplying by the equivalent molecular weights and recalculating to a sum of 100.

REFERENCES

- AHRENS, L. H. (1957), A survey of the quality of the principal abundance data of geochemistry: *Physics and chemistry of the earth*, **2**, 30-45.
- BARTH, T. F. W. (1952), *Theoretical petrology*. John Wiley & Sons, Inc., New York, 387 p.
- FAIRBAIRN, H. W., SCHLECHT, W. G., STEVENS, R. E., DENNEN, W. H., AHRENS, L. H. AND CHAYES, F. (1951), A co-operative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks: *U. S. Geol. Surv. Bull.*, **980**, 57 p.
- FRIEDMAN, G. M. (1960), Chemical analyses of rocks with the petrographic microscope: *Am. Mineral.* **45**, 69-78.
- NIGGLI, P. (1936), Über Molekularnormen zur Gesteinsberechnung: *Schweiz. mineral. petrog. Mitt.*, **16**, 295-317.