# DERIVATION OF MINERAL FORMULAS FROM THE CHEMICAL ANALYSES OF MINERALS BY COMPUTER.

*Mohammad Majid*

## ABSTRACT

The procedure for deriving formula and atomic ratios from the analyses of feldspar, tri-octahedral micas and pyroxene has been programmed in FORTRAN IV for a 1904 A/7600 computer. The method outlined by Deer, Howie and Zussman (1971) has been followed in calculating the numbers of ions per formula unit. Part of the program dealing with the analytical data of tri-octahedral micas has been designed on the basis of cationic and anionic valence content of the idealized unit cell, 44 (22 in half cell) because of the uncertainty of F,Cl,;and $H_2O$ contents in most analyses, specially those obtained with electron probe. In addition to the numbers of ions per formula, the comudter printout of calculation includes a derived structural formula expressed in a fashion outlined by Heinrich (1946) and Deer et al. (1967). The arrangement of groups and cations within each group in the formula is after Foster (1960). Several extra numerical arrays were entered in the program to recognize the partition of $R^{+3}$ cations in tetrahedral and octahedral coordination categories. The program has been written for the research workers who frequently deal with the analytical data of minerals. Comparison has been made with the computer-based procedure of Jackson, Stevens and Bowen (1967) for deriving structural formula from mineral analyses.

## Calculation of the numbers of ions per formula unit.

There have been generally two ways of calculating the numbers of ions per mineral formula. Miser and Stevens (1938) used the anion-based, hydrogen -equivalent method in determining the composition of taeniolite and later applied to other micas by Stevens (1938, 1945). The procedure was generalized for application to all minerals by Jackson *et al.* (1967). These authers also formulated a program in Extended Algol for the Burroughs B 5500 computer.

In the anion-based, hydrogen-equivalent method, weight percentages of the constituent oxides are divided by their respective equivalent weights to obtain the number of equivalents per hundred weight. These values are normalized to twice the numbers of anions in the type formula, in order to get the number of equivalents per formula. The numbers of ions per formula are calculated in turn, by dividing the number of equivalents per formula by the valence of the ions concerned (Hurlbut, 1959).

The method adopted in the present program consists of calculating set of numbers proportional to the number of oxygen atoms associated with each of the element in the concerned oxides. From the atomic proportions of oxygen, after being made equal to the number of anions in the type formula, the ions per formula unit are obtained by dividing these on the number of oxygens associated with one cation in the constituent oxides.

Table 1 shows composition of a clinopyroxene analysed with electron probe from hypersthene diorite, Comrie diorite complex, Scotland. Calculation of numbers of ions according to the type formula $X_{1-}p\ Y_{1+}p\ Z_2O_6$ from the represented chemical analysis will illustrate the method adopted in the program. From the weight percentages of the constituent oxides in col. 1, molecular proportions have been determined. Column 2 is derived, therefore, by dividing each column 1 entry by the molecular weight of the oxide concerned. The molecular proportions of the constituent oxides are next multiplied by the number of oxygen atoms in that oxide. Column 3 thus gives a set of numbers proportional to the number of oxygen atoms associated with each of the elements expressed as oxide in the analysis. The atomic proportions of oxygen are next multiplied by the normalizing factor to give numbers whose total balance the anions ( 6 oxygens) in the type formula. From the normalized values of oxygens in column 4, the numbers of the associated cations have been determined and are listed in column 5.

**TABLE** 1. Calculation of the numbers of ions on the basis of 6 oxygens. Diopsidic-augite, Comrie diorite complex, Scotland (Majid, 1974).

| Oxides | 1 Weight percentages | 2 Mol.Prop. of oxides | 3 Atom.Prop. of oxygen from each mol. | 4 Normalized values | 5 Nos. of ions in the formula |
|---|---|---|---|---|---|
| $SiO_2$ | 52.32 | 0.8706 | 1.7412 | 3.9264 | 1.96 |
| $Al_2O_3$ | 1.95 | 0.0191 | 0.0573 | 0.1292 | 0.09 |
| $Fe_2O_3$ | | ......... | ......... | ......... | ...... |
| FeO | 10.24* | 0.1425 | 0.1425 | 0.3213 | 0.32 |
| MgO | 14.70 | 0.3645 | 0.3645 | 0.8219 | 0.82 |
| CaO | 19.62 | 0.3498 | 0.3498 | 0.7887 | 0.79 |
| $Na_2O$ | 0.31 | 0.0050 | 0.0050 | 0.0113 | 0.02 |
| $TiO_2$ | 0.82 | 0.0102 | 0.0204 | 0.0460 | 0.03 |
| $K_2O$ | 0.00 | ......... | ......... | ......... | ...... |
| MnO | 0.00 | ......... | ......... | ......... | ...... |
| $H_2O^-$ | 0.00 | ......... | ......... | ......... | ...... |
| $H_2O^+$ | 0.00 | ......... | ......... | ......... | ...... |
| Total | 99.96 | | | | |

*total iron expressed as FeO.

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SPECIMEN  NO    18

CHEMICAL  COMPOSITION

      SIO2=52.58

    AL2O3= 1.16

      FEO= 8.98

     MGO=15.35

     CAO=21.30

    NA2O= 0.00

     TIO2= 0.48

      K2O= 0.00

     MNO= 0.00
  TOTAL  =99.85

NUMBER OF THE IONS ON THE BASIS OF THE 6 OXYGENS
  SI  =1.958

 AL  = .051

  TI  = .013

 MG  = .852

 CA  = .850

 NA  =0.000

 FE  = .280

  K  =0.000

 MN  =0.000

TOTAL=4.003

        ATOMIC  PERCENT  CA  =  42.89
        ATOMIC  PERCENT  MG =  42.99
       ATOMIC PERCENT FE+MN =  14.11
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**Figure 1.** Computer printout of calculation for an augite, analaysed by electron probe.

Comparison of the adopted method has been made with the anion-based, hydrogen-equivalent procedur in table 2. Chemical analysis of a calcic-labradorite, published by Stewart *et al.* (1966) which was selected by Jackson *et al.* (1967) as an illustration of their computer-based procedure, has been processed according to the described method. The results are shown in column 5 of table 2.A. Table 1 of the Jackson *et al.*'s work (C24, 1967) has been reproduced here for comparison. It is evident that the numbers of the various ions per formula unit in both cases are exactly similar no matter what method has been used for calculation.

**PROGRAM:**

This program, though constructed on fixed-anion basis, is so designed that in case of minerals with complex formula, the calculation sheet exhibits the derived structural formula with grouping of ions in their proper coordination categories. Determination of various useful ionic ratios has also been a part of the program. The analytical data is punched on the input-data cards. Each sample data is included on individual cards. The constituent elements, expressed as oxides, are entered on the input-data cards in the following order. 1. $SiO_2$. 2. $Al_2O_3$ 3. $Fe_2O_3$ 4. FeO 5. MgO 6. CaO 7. $Na_2O$ 8. $TiO_2$ 9. $K_2O$ 10. MnO 11. $H_2O^-$ 12. $H_2O^+$.

The FORMAT (I5, 12 F5.2) statement of the program defines how the data is punched on the cards. The user selects the appropriate number of anions per formula and enters it in the field specified by the field descriptor, I5. In the remaining columns, the analytical data is recorded in the above mentioned order in fixed point formate in 12 fields; each field being 5 characters wide, two of these are after the decimal. The first data card registers number of the samples according to the format associated with the first READ statement. If number of the samples exceeds three digits (e.g. 999), FORMAT (I3) should be altered to the desired value.

From the input - data cards computer first lists out the individual oxides (top of the fig.1), determines their total and records it at the bottom of the analysis on the printout sheet. The weight percentages of oxides are then divided by their respective mol. weights (mol. weights are calculated from the 1961 revised atomic weights of the Commission on Atomic Weights of the International Union of Pure and Applied Chemistry: Cameron and Wichers, 1962) to obtain the molecular proportions of the oxides.

These values are next normalized to sets of numbers proportional to the numbers of oxygen atoms associated with each of the elements in the concerned

**TABLE 2.** Comparison of the adopted method with the anion-based, hydrogen - equivalent procedure of calculating ions per formula.

[Calcic labradorite, Lake county, Oregon. (Stewart and other, 1966): Type formula $W_4Z_{16}O_{32}$]

**A.** Example of the adopted method for calculating the number of ions on the basis of 32 oxygens.

| Oxides | 1 Wt% of oxides | 2 Mol. Prop. of oxides | 3 Atom. Props. of oxygen from each mole | 4 Normalized values | 5 Nos. of ions in formula. |
|---|---|---|---|---|---|
| $SiO_2$ | 51.42 | 0.8557 | 1.7114 | 18.7294 | 9.3647 |
| $Al_2O_3$ | 30.46 | 0.3017 | 0.9051 | 9.9053 | 6.6035 |
| $Fe_2O_3$ | 0.24 | 0.0015 | 0.0045 | 0.0492 | 0.0328 |
| $TiO_2$ | 0.04 | 0.0005 | 0.0010 | 0.0109 | 0.0054 |
| MgO | 0.05 | 0.0012 | 0.0012 | 0.0131 | 0.0131 |
| FeO | 0.17 | 0.0024 | 0.0024 | 0.0263 | 0.0263 |
| CaO | 13.42 | 0.2393 | 0.2393 | 2.6188 | 2.6188 |
| $Na_2O$ | 3.52 | 0.0567 | 0.0567 | 0.6205 | 1.2410 |
| $K_2O$ | 0.23 | 0.0024 | 0.0024 | 0.0263 | 0.0526 |
| $H_2O^-$ | 0.04 | | | | |
| Total | 99.89 | | | | |

Continued Table 2.

B. Example of the anion—based hydrogen - equivalent method of ealculating ions per formula.

| Oxides | 1<br>Weight percentages | 2<br>Wt. of one equivalent | Ions | 3<br>Equivalent per hundred weight | 4<br>Equivatents per formula | 5<br>Ions per formula |
|---|---|---|---|---|---|---|
| $SiO_2$ | 51.42 | 15.021 | $S_1^{+4}$ | 3.4232 | 37.459 | 9.365 |
| $Al_2O_3$ | 30.76 | 16.9935 | $Al^{+3}$ | 1.8101 | 19.808 | 6.603 |
| $Fe_2O_3$ | 0.24 | 26.615 | $Fe^{+3}$ | 0.0090 | 0.099 | 0.033 |
| $TiO_2$ | 0.04 | 19.97 | $Ti^{+4}$ | 0.0020 | 0.022 | 0.006 |
| MgO | 0.05 | 20.156 | $Mg^{+2}$ | 0.0025 | 0.027 | 0.014 |
| FeO | 0.17 | 35.923 | $Fe^{+2}$ | 0.0047 | 0.051 | 0.026 |
| CaO | 13.42 | 28.04 | $Ca^{+2}$ | 0.4786 | 5.237 | 2.619 |
| $Na_2O$ | 3.52 | 30.9895 | $Na^{+1}$ | 0.1136 | 1.243 | 1.243 |
| $K_2O$ | 0.23 | 47.102 | $K^{+1}$ | 0.6049 | 0.054 | 0.054 |
| $H_2O^-$ | 0.04 | ………… | ……… | ………… | ………… | ………… |
| Total | 99.89 | ………… | ……… | 5.8486 | 64.000 | 19.963 |
| Anions | ………… | ………… | $O^{-2}$ | 5.8486 | —64.000 | —32.000 |

oxide. The computer reads the required number of anions per formula and recasts the oxygen atom proportions so that they total the number, defined by the first field descriptor in the input-data. The remaining part of the program deals with the determination of the exact no. of ions per formula, grouping of ions in their proper coordination categories, printing out the derived structural formula and calculation of the important atomic ratios.

In majority of the silicate minerals the only anion present is oxygen or (OH). The constituent elements are determined and expressed conventionally as wt.percentage of oxides although the oxides do not exist as such in minerals. The procedure adopted in the present work is justifiable, since each element can be though of as associated with its appropriate share of the oxygen atoms in the crystal structure (Deer, Howie and Zussman, 1971).

**Example of calculation.**

**Tri-octahedral micas.** The program involves the calculation of ions per formula on the basis of cationic and anionic valence content of the idealized unit cell, 44 (22 in half cell formula) as mentioned earlier. In the derived structural formula, printed below the ions per formula (fig.2) $R^{+3}$ are partitioned between the tetrahedral and octahedral coordinated groups. The number of ions of $Al^{+3}$ was insufficient to make up the total of 4 cations in the tetrahedral coordination in the given example. The unoccupied tetrahedral structural positions are being filled successively by assigning ions of $Fe^{+3}$ and in extreme cases by $Ti^{+4}$ to the IV coordination structural sites untill all such positions total the desired value. Several numerical arrays have been entered in the part of program dealing with processing of the tri-octahedral micas' analytical data for this purpose. There are objections to this practice from the theoritical considerations that ions having radii larger than $Al^{+3}$ ($>$0.51 Å.) consistantly do enter IV-coordination lattice positions. Foster (1960) has, however, pointed out the possibility of substitution of $Al^{+3}$ and other $R^{+3}$ ions for Si in the IV-coordinated structural positions. From the study of compositions of a large number of tri-octahedral micas, it was concluded that the extrapositive charge, induced on the octahedral layer due to the proxying of trivalent for bivalent ions, is accommodated partly by the negative charges associated with the unoccupied octahedral positions and partly by the increase negative tetrahedral charge owing to the greater substitution of $R^{+3}$ for Si.

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    SPECIMEN NO        5
    CHEMICAL COMPOSITION
   SIO2=39.72

 AL2O3=13.01

 FE2O3= 5.73

   FEO= 8.40

  MGO=16.83

  CAO=  .04

 NA2O=  .17

  TIO2= 3.26

  K2O= 9.58

  MNO= 0.00

 H2O-= 0.00

 H2O+= 0.00

TOTAL =96.74

     NUMBER OF THE IONS ON THE BASIS
     OF THE 22 OXYGENS.
     SI= 5.740

     AL= 2.216

     TI=  .354

  FE***=  .623

     MG= 3.624

     CA=  .006

     NA=  .048

   FE**= 1.015

      K= 1.766

     MN= 0.000

TOTAL =15.393
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**Figure 2.** Computer printout of calculation for a biotite from diorite.

Continued Fig. 2.

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(SI=2.87 AL=1.11 FE ***= .O2)  (FE ***= .29 TI= .18FE**= ·51 MG
=1.81 MN=0.00)  O10  (OH)2     (K=.88NA=.02CA/2=.00).

            ATOMIC  RATIOS

            FE***=11.84

            FE** =19.29

            MG  =68.87

            FE/FE+MG·100=31.13

            OCTAHEDRAL  OCCUPATION  =2.79

            FE**+MN** Percent in octahedral group =18.22

            MG  Percent in octahedral group =65.03

            R+3 Cations percent in octahedral group =16.75
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Cases are there when the extrapositive charge on the octahedral group is balanced wholly by the negative charges associated with the unoccupied octahedral positions or completely by the excess negative charge on the tetrahedral group.

The percentages of $Fe^{+3}$, $Fe^{+2}$ and Mg, and $(\frac{Fe}{Fe+Mg} \times 100)$ ratios have been determined. Details of the octahedral layer are also included on the printout of calculations of each specimen.

**Pyroxene.**

The program gives the following informations from the analysis of pyroxene.

1. Number of ions on the basis of 6 oxygens.
2. Atomic pereent Ca, Mg, and Fe+Mn.
3. $a^{pxn}_{Mg_2Si_2O_6}$
4. $X^{pxn}_{Fe}$

$a^{pxn}_{Mg_2Si_2O_6}$ is the activity of enstatite in a particular pyroxene which equals

$Y(M1).\ Y(M2).\ \left(\frac{Mg}{Mg+Fe}\right)^2_{pxn}$. Y(M1) and Y(M2) are M1 and M2 sites that remain after subtracting the occupancies of these sites by the octahedrally coordinated ions, assuming that the large ions like $Ca^{+2}$, $Na^{+}$ and $Mn^{+2}$, present in the ortho and clinopyroxene structure, occupy M2 while the smaller octahedrally coordinated ions like $Al^{+3}$, $Cr^{+3}$ and $Ti^{+4}$ occupy M1 site.

$$X^{pxn}_{Fe} = \left(\frac{Fe^{+2}}{Fe^{+2} + Mg^{+2}}\right)_{pxn}$$

Ratios 3 and 4 are important in the determination of the temperature of formation (crystallization) of rocks, using analyses of the co-existing pyroxenes. From study of the equilibrium relations along the $MgSiO_3$ – $CaMgSi_2O_6$ join of the pyroxene quadrilateral (Boyd, 1964), it is evident that the solubility of enstatite in the clinopyroxenes is temperature dependant. Wood and Banno (1973) made an empirical approach to the enstatite solubility in complex clinopyroxene and developed a formula which enables the equilibration temperatures to be calculated with a fair degree of accuracy, provided analyses of the co-existing pyroxenes are available.

$$T = \frac{-10202}{2.303 \log_{10} \left\{\frac{a^{cpx}\ Mg_2\ Si_2O_6}{a^{opx}\ Mg_2\ Si_2O_6}\right\} - 7.65\ X^{opx}_{Fe} + 3.88\ (X^{opx}_{Fe})^2 - 4.6}$$

T is the temperature of equilibration in K°

**Feldspar.** The analytical data is processed by computer according to the type formula $W_4Z_{16}O_{32}$. Calculation of the Wt. % Ab, Or, and An components is also a part of the program. Fig.3 is a print of the calculation sheet of an andesine analysed by wet chemical methods. The chemical composition is printed at the top. The wt % Ab, Or, and An have been calculated and listed below the numbers of ions per formula, with their total, added at the bottom. The closeness of the sum of wt % Ab+Or +An to the theoritical value (approx.100) is a good check on the high quality of the andesine analysis under consideration. Deficiencies in the calculated values of wt % Ab + Or + An from the analysis of feldspar by more than approx. 4–5% clearly indicate analytical error. The recalculated to 100 values of the three feldspar components are printed below their actual percentage.

**Note.** The program can be used for interpretation of the compositions of clinopyroxene, orthopyroxene, tri-octahedral micas, plagioclase and alkali feldspar. It will be generallized soon for application to other minerals. Copy of the program may be obtained from the author.

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SPECIMEN  NO           1
CHEMICAL  COMPOSITION

 SIO2=58.07

AL2O3=26.57

FE2O3= 0.00

  FEO=  .32

  MGO=  .01

  CAO= 7.69

 NA2O=6.76

 TIO2=  .02

  K2O=  .48

  MNO= 0.00

 H2O-= 0.00

 H2O+= 0.00

TOTAL   =99.92
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**Figure 3.** Computer printout of calculation for an andesine.

Continued Fig. 3.

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NUMBER OF THE IONS ON THE BASIS OF THE 32 OXYGENS

   SI   =10.408
   AL  = 5.614
   TI   =  .003
FE***  = 0.000
   MG =  .003
   CA  = 1.477
   NA  = 2.549
 FE**   =  .048
   K    =  .110
   MN = 0.000
TOTAL  =20.012


   WT    PERCENT  AB  =  57.20
   WT    PERCENT  OR  =   2.84
   WT    PERCENT  AN  =  38.14
   TOTAL  = 98.18


   RECALCULATED TO 100

   WT    PERCENT  AB  =  58.26
   WT    PERCENT  OR  =   2.89
   WT    PERCENT  AN  =  38.85
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