

# Mineral Formulae

## Level 2 Computing — Project 4:

### Project Abstract

This project is an example of data handling, data evaluation and data plotting of the kinds of analyses that you can obtain from the electron microprobe. The objective will be to take six amphibole analyses and determine what kind of amphiboles they are. This may appear simple, but, accomplishing this task requires more effort than you may imagine. In Project 4 you will:

- (1) use EXCEL to calculate all-ferrous mineral formulae for 6 amphibole analyses,
- (2) make site assignments for the cations you have determined for these analyses,
- (3) use EXCEL to estimate maximum, minimum and mean values for ferric iron in your analyses (note: average = arithmetic mean, I may use these interchangeably in subsequent text),
- (4) make site assignments for the cations you have determined for the mineral formulae,
- (5) classify the amphiboles and plot for the AVERAGE ferric formulae in DELTAGRAPH on the two diagrams (E and F) indicated on page 10.
- (6) edit the DELTAGRAPH file in ILLUSTRATOR if necessary. I am expecting **publication quality** figures.

You will be supplied with an EXCEL file (Amphibole.xls) with chemical analyses of 6 amphiboles and EXCEL templates for the calculation of the analyses and the site assignments.

### The assignment

Download the EXCEL workbook from the website at the level 2 DIY computing page.

overwritten. (2) Use the instructions below to work through each of the five worksheets in sequence in the **Amphibole.xls** workbook. As an aid, there are references on the worksheets to the instructions below.

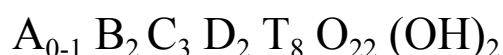
Most of the rest of this document is a step-by-step description of a worked example of calculations you are being asked to do. Some of this material may be unfamiliar, but try to work through this with others in your year.

## Background

The electron microprobe is most widely used method to determine the chemical composition of minerals; however, the electron microprobe cannot distinguish among the valence states of elements. This is unfortunate because it is clear that most amphiboles contain at least some ferric iron — see compilations of Leake (1968) and Robinson *et al.* (1982). Additionally, the pleochroism displayed by many amphiboles in thin section is further evidence that ferric iron is present in the amphibole. Consequently, there is a need to estimate empirically ferric contents of amphiboles.

### *The Amphibole Group*

Double chains of silicate tetrahedra with the general formula:



Cations that commonly are found at these five sites

**A:** Na<sup>+</sup>, K<sup>+</sup>

**B:** Na<sup>+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>

**C:** Mg<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>

**D:** Al<sup>3+</sup>, Fe<sup>3+</sup>, Ti<sup>4+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>

**T:** Si<sup>4+</sup>, Al<sup>3+</sup>

Examples: Ca<sub>2</sub> Mg<sub>3</sub> Mg<sub>2</sub> Si<sub>8</sub> O<sub>22</sub> (OH)<sub>2</sub> - tremolite; A = 0, here.

Na Ca<sub>2</sub> Mg<sub>3</sub> Mg<sub>2</sub> Si<sub>7</sub> AlO<sub>22</sub> (OH)<sub>2</sub> - edenite; A = 1, here.

### *Empirical estimates of ferric iron*

Empirical estimates of ferric iron are calculations that are based on knowledge of mineral stoichiometry. These estimates are not just poor approximations that suffice in the absence of analytical determinations of ferric-ferrous ratios. Empirical estimates yield exactly the same results as analytical determinations of ferric iron, if (1) the analysis is complete (total Fe plus all other elements), (2) the analytical determinations are accurate and (3) the mineral stoichiometry (ideal anion and cation sums) is known. In the case of amphiboles, condition (3) cannot be uniquely determined because the *A*-site occupancy varies. However, knowledge of amphibole stoichiometry and element distribution can be used to estimate a range of permissible structural formulae and ferric contents **[Note: In project 4 you will not be concerned with this]**.

The most welcome circumstances will be where the difference between the limiting structural formulae are trivial, and the entire range plots within the same classification field. However, there will also be cases where the range of stoichiometrically allowable formulae is broad and spans two or more fields in the classification. **[Note: In project 4 you may observe this]**.

The procedure of estimating ferric iron will require at least one recalculation of the **all-ferrous** analysis to a different cation sum. Consequently, familiarity with calculation of mineral formulae is highly recommended for a fuller understanding of the ferric estimation procedure. Thorough discussions of the calculation of mineral formulae can be found in the appendices of Deer *et al.*, (1966, 1992) and in the appendix of Leake *et al.* (1997). The topic of ferric estimates in amphiboles has been discussed by Stout (1972), Robinson *et al.* (1982, p. 3 - 12), Droop (1987), Jacobson (1989), J. Schumacher (1991) and Holland and Blundy (1994).

### **An example of the recalculation of an electron microprobe analysis and the procedure for estimating minimum, maximum and mean ferric contents**

In the example below:

**Steps 1 through 4** that are described below describe the type of calculation necessary to obtain a mineral formula from a chemical analysis.

**Step 5** is an example of how to make site assignments in amphiboles using the cation proportions that were calculated in Steps 1 through 4.

**Steps 6 - 13** show the criteria for determining the minimum, maximum and mean estimates of ferric Fe for an amphibole analysis.

**Worked Example:**  
**Calculation of a Mineral Formula and a Ferric Estimate from an Electron Microprobe Analysis of an Amphibole**

**Note:** For the description, columnar table layout below is appropriate, but it is not efficient for an EXCEL worksheet layout)

As an example (Table 2), the analysis that appears in Deer *et al.* (1992, p. 678) was chosen. To simulate analysis by electron microprobe the ferric iron was recast as ferrous iron and the water analysis was ignored. The ferric estimate was made assuming 2 (OH) are present rather than the 2.146 suggested by the actual water determination. Any discrepancies in the final decimal places of the numbers that appear below and in Table 2 are due to rounding effects.

	1	2	3	4	5	6
	wt%	Molecular Proportions	Atomic Proportions (cations)	Atomic Proportions (oxygens)	anions on the basis of 23 oxygens	cations on the basis of 23 oxygens
		wt% + mol. wt.	col. 2 × cations in oxide	col. 2 × oxygens in oxide	col. 4 × 8.45012	col. 3 × 8.45012
SiO <sub>2</sub>	51.63	0.85928	0.85928	1.71857	14.52208	7.261
TiO <sub>2</sub>	0.00	0.00000	0.00000	0.00000	0.00000	0.000
Al <sub>2</sub> O <sub>3</sub>	7.39	0.07248	0.14496	0.21744	1.83736	1.225
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00000	0.00000	0.00000	0.00000	0.000
FeO	7.55	0.10509	0.10509	0.10509	0.88799	0.888
MnO	0.17	0.00240	0.00240	0.00240	0.02025	0.020
MgO	18.09	0.44884	0.44884	0.44884	3.79274	3.793
CaO	12.32	0.21969	0.21969	0.21969	1.85641	1.856
Na <sub>2</sub> O	0.61	0.00984	0.01968	0.00984	0.08317	0.166
K <sub>2</sub> O	0.00	0.00000	0.00000	0.00000	0.00000	0.000
sum			1.79994	2.72185	23.0000	15.209

Factor for the recalculation of atomic proportions to 23 O basis: $23 \div 2.72185 = 8.45012$
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**Note:** Remember that numbers from this and the following tables may vary slightly do to slight differences in rounding.

- (1) Divide each wt% (column 1) by the molecular wt of the oxide to yield the *molecular proportion* of each oxide (column 2). [e.g., for SiO<sub>2</sub>:  $51.63 \div 60.085 = 0.85928$ ]. Data from Robie *et al.*, (1978) were for the molecular weights in this example.
- (2) Obtain *atomic proportions of the cations* (column 3) and *atomic proportions of the oxygens* (column 4) by multiplying each *molecular proportion* value by the number of cations and oxygens in the oxide. [e.g., for SiO<sub>2</sub>:  $0.85928 \times 1 = 0.85928$  and  $0.85928 \times 2 = 1.71857$ ].

Note: Assuming 2 (OH) groups are present, 1 oxygen is balanced by 2 H (i.e., H<sub>2</sub>O) so the cation charges are balanced by the remaining 23 oxygens which is the basis of the anhydrous amphibole formula (see text for discussion: it can be shown that, even if F and Cl have not been determined, as long as OH+F+Cl = 2 the 23 oxygen formula will give the correct mineral formula).

- (3) Obtain the *anions based on 23 oxygens* (column 5) by multiplying each value in column 4 by (23 divided by the sum of column 4) [e.g.,  $23 \div 2.72185 = 8.45012$ ; for SiO<sub>2</sub>:  $1.71857 \times 8.45012 = 14.52208$ ].
- (4) Obtain the *cations on the basis of 23 oxygens* (column 6) by multiplying each value in column 3 by  $23 \div$  the sum of column 4 [e.g., for SiO<sub>2</sub>:  $0.85928 \times 8.45012 = 7.261$ ]

Note : Column 6 is the all-ferrous mineral formula for the amphibole. Assigning the cations to sites shows if any deviations from ideal stoichiometry can be explained by failure to account for ferric iron.

ideal site assignments	7	cations	8	9
	Min. formula from col. 6		col. 6 $\times$ 0.99714	col. 8 $\times$ oxygen per cation
Si	7.261			
Al <sup>IV</sup>	0.739			
sum T	8.000	Si	7.2401	14.4802
Al <sup>VI</sup>	0.486	Al	1.2214	1.8321
Fe <sup>3+</sup>	0.000	Ti	0.0000	0.0000
Cr	0.000	Cr	0.0000	0.0000
Mg	3.793	Mg	3.7818	3.7818
Fe <sup>2+</sup>	0.721	Fe <sup>2+</sup>	0.8854	0.8854
Mn	0.000	Mn	0.0000	0.0000
sum C	5.000	Ca	1.8511	1.8511
Mg	0.000	Na	0.1652	0.0829
Fe <sup>2+</sup>	0.167	K	0.0000	0.0000
Mn	0.020	sum	15.1653	22.0337
Ca	1.856	<div style="border: 1px solid black; padding: 10px; margin: 10px 0;"> <math>\Sigma \text{Ca (col. 7)}</math>  <math>15 \div 15.043 = 0.99714</math>  <math>(23 - 22.9337) \times 2 = 0.1326</math>  <math>0.885 - 0.133 = 0.753</math> </div>		
Na	0.000			
sum B	2.043			
Na	0.166			
K	0.000			
sum A	0.166			
<b>total</b>	<b>15.209</b>			

Note : The procedure to this point would apply to any mineral

- (5) Ideal site assignments (column 7) are made from the cation values in column 6 — a general procedure is:

(a) *the 8 tetrahedral (T) sites:*

- place all Si here, if Si < 8 fill the remaining sites with Al.
- if Si + total Al < 8, then place all Si + Al here

(b) *the 5 octahedral (C) sites (M2, M1, M3)*

- place Al remaining from step (a), Ti, Fe<sup>3+</sup> (initially = 0), Cr and here. In the following order, place enough Mg, Fe<sup>2+</sup> and Mn to bring the total to 5.
- if  $\sum(\text{Al}^{\text{VI}} \dots \text{Mn}) < 5$ , then place all these elements here

(c) *the 2 (B) sites (M4)*

- place any Mg, Fe<sup>2+</sup> or Mn and Ca remaining after step (b) here
- if  $\sum(\text{Mg} \dots \text{Ca}) \text{ at } B < 2$ , fill the remaining sites with Na to bring the total to 2

(d) *the single large (A) site*

- place any remaining Na and K here

**Note:** Step 5 applies to assigning cations to sites amphiboles, but this is commonly done for all minerals

**Note:** The next steps deal specifically with estimating the amount of ferric Fe in amphiboles

- (6) Evaluating the structural formula

If any site has less than their ideal values ( $T=8.000$ ,  $C=5.000$ ,  $B=2.000$ ,  $A=0.000$  to  $1.000$ ), then a ferric estimate is either impossible or only possible with additional constraining information. This could also indicate an analytical problem.

Go to next page

ideal site assignments	1 0	1 1	1 2	1 3
	Formula (15eNK) minimum Fe <sup>3+</sup>	Formula (15eK) maximum Fe <sup>3+</sup>	Formula Average of Min. and Max. Fe <sup>3+</sup>	Formula from DHZ
Si	7.240	7.161	7.201	7.196
Al <sup>IV</sup>	0.760	0.839	0.799	0.804
sum T	8.000	8.000	8.000	8.000
Al <sup>VI</sup>	0.462	0.369	0.416	0.410
Fe <sup>3+</sup>	0.133	0.634	0.383	0.263
Cr	0.000	0.000	0.000	0.000
Mg	3.782	3.740	3.761	3.759
Fe <sup>2+</sup>	0.624	0.242	0.440	0.618
Mn	0.000	0.015	0.000	0.000
sum C	5.000	5.000	5.000	5.000
Mg	0.000	0.000	0.000	0.000
Fe <sup>2+</sup>	0.129	0.000	0.057	0.050
Mn	0.020	0.005	0.020	0.020
Ca	1.851	1.831	1.841	1.840
Na	0.000	0.164	0.082	0.090
sum B	2.000	2.000	2.000	2.000
Na	0.166	0.000	0.083	0.074
K	0.000	0.000	0.000	0.000
sum A	0.166	0.000	0.073	0.074
total	15.166	15.000	15.083	15.074

The suitability of the analysis for a ferric estimation and the normalizations that yield the maximum and minimum estimates of ferric iron can be determined by calculating the normalization factors for all the various stoichiometric and chemical limits. These are given below and are obtained from columns 6 or 7.

limit	calculation method	calculation	normalization factor
<i>Calculations for minimum ferric estimates</i>			
8Si	8÷Si	8÷7.261	1.1018
16CAT	16÷ΣK	16÷15.210	1.0519
all ferrous	—	—	1.0000
15eNK	15÷ΣCa	15÷15.043	0.9971*
<i>Calculations for maximum ferric estimates</i>			
15eK	15÷ΣNa	15÷15.210	0.9862*
13eCNK	13÷ΣMn	13÷13.187	0.9858
all ferric	23÷ [23 + (0.5 × Fe <sup>2+</sup> )]	23÷23.444	0.9811
10ΣFe <sup>3+</sup>	36÷ (46-Si-Al-Ti-Cr)	36÷37.5141	0.9596
8SiAl	8÷ΣAl	8÷8.486	0.9427

\* Indicates normalizations that yield either the minimum or maximum ferric estimates

If the all the normalization factors (8Si, 16CAT and 15eNK) are greater than all the normalization factors (8SiAl, 15eK, 10 $\Sigma$ Fe<sup>3+</sup> and 13eCNK), then a minimum and a maximum ferric estimation can be calculated; if not, then no estimation is possible.

**(7) Minimum ferric estimates**

The lowest normalization factor among the four choices, 8Si, 16CAT, 15eNK and all ferrous, determines the formula that yields the minimum ferric estimate. If the factors 8Si, 16CAT and 15eNK are all greater than 1.0000, then the all-ferrous formula (Fe<sup>3+</sup> = 0.000) is the lower limit. In this example, the 15eNK-normalization factor is the lowest.

To obtain the formula that gives the minimum ferric estimate (column 8), multiply the cations from column 6 by the 15eNK-normalization factor 0.99714 (15 ÷ 15.043).

- (8)** Find the sum of oxygen (22.9337) in the normalized formula by multiplying each single cation value (column 8) by the number of balancing oxygens [e.g. for SiO<sub>2</sub>,  $7.2401 \times 2 = 14.4802$ ; for AlO<sub>1.5</sub>,  $1.2214 \times 1.5 = 1.8321$ ; for MgO,  $3.7818 \times 1 = 3.7818$ ; for NaO<sub>0.5</sub>,  $0.1659 \times 0.5 = 0.0829$ ]
- (9)** *Ferric Fe* equals the amount of ferrous Fe the must be converted to bring the total oxygens up to 23. The amount is  $(23 - 22.9337) \times 2 = 0.133$ .
- (10)** The *new ferrous Fe* value is the total Fe from column 8 minus the ferric Fe. [e.g.  $0.885 - 0.133 = 0.753$ ]
- (11)** Recast the normalized cations as in step 5 (column 10). This should yield a formula with no violations of the ideal stoichiometry.

**Note:** Step 11 is double checks the correctness of your calculations. It also is a check of whether correcting the initial stoichiometric violation will produce another [here, insufficient cations to fill *T* or *C* could result from the 15eNK normalization. Such analyses cannot be used for ferric Fe estimates (unfortunately, a lot of calculating is involved in determining this)].

**(12) Maximum ferric estimates**

The largest normalization factor among the four choices, 8SiAl, 15eK, 13eCNK and all ferric, determines the formula that yields the maximum ferric estimate. If the factors 8SiAl, 15eK and 13eCNK are all less than the all-ferric value, then the all-ferric formula would give the maximum Fe<sup>3+</sup>. In this example, the 15eK normalization factor is the largest and can be used to gives the formula with maximum Fe<sup>3+</sup>.

To obtain the formula that gives the maximum ferric estimate (column 11), repeat steps 7 through 10 for using the 15eK normalization factor 0.98621 (15 ÷ 15.210).

**(13) Average of the maximum and minimum ferric estimates**

To obtain the formula that gives the average of the maximum and minimum ferric estimates (columns 10 and 11), repeat steps 7 through 10 for using the average of the normalization factors that were obtained in steps 7 and 12. This normalization factor is 0.99167  $[(0.99714 + 0.98621) \div 2]$ .



- (14) The actual formula (column 12) given in Deer et al. (1992) lies approximately between the minimum (15eNK) in column 10 and maximum (15eK) in column 11, but is nearer to the minimum.

## References

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- Stout, J. H. (1972) Phase petrology and mineral chemistry of coexisting amphiboles from Telemark, Norway. *Journal of Petrology* 13, 99-145.

**THE NEXT PAGE GIVES THE FORMATS AND INFORMATION FOR THE PLOTS**