

## SETTING UP MINERAL NORMALIZATIONS IN EXCEL

### The almost-exhaustive "how to derive mineral formulas from chemical analyses"

These instructions describe, in fair detail, how to set up mineral normalizations for a variety of minerals. This will be done using a spreadsheet program such as MS Excel. Each row will represent an individual analysis; the calculations are done across the columns.

1. Save the first column for any identifying or descriptive information about the analyzed spot. This column can be labeled "description".

description			F	Na
test of chromian augite standard	cpx		0.023	
B. del Cerro cpx	cpx		0	0.
B. del Cerro, adj cpx	cpx		0.01	0.
B. del Cerro, cpx			0.007	0.
B. del Cerro, cpx			0	0.
B. del Cerro, cpx			0.029	0.
CNN, cpx			0.155	0.
Nord mine cpx	cpx - Ca		0.975	1.
Nord mine pyx	cpx - Ca		0.614	0
Nord mine opx ?	opx		0.368	0.
Nord mine pyx	opx		0.394	0.
Nord mine pyx	opx		0.437	0.

Additional columns with information such as analysis date, locality, thin section and spot number, associated minerals, or other information may also be useful.

2. In the next set of columns, list the raw weight% values from the microprobe. Don't worry about oxygen, OH, what the valence of any Fe might be, or any other information you don't know at this point; simply tabulate the elements you actually measured. I find it useful to have the elements arranged in some logical sequence, such as by increasing atomic number.

corrected raw weight percent								
F	Na	Mg	Al	Si	P	S	Cl	
0.142	2.00294	7.456	7.265	18.893	0.016	0.024	0.031	
0.155	0.381	10.852	1.446	25.434	0	0	0.063	
0.102	0.16	9.499	0.661	25.521	0	0.015	0.014	
0.088	0.13685	9.626	0.795	25.15	0	0.085	0.024	
0.279	0.19291	9.35	0.726	25.819	0	0	0.098	
0.095	0.3997	9.933	1.214	25.465	0	0	0.061	
0.064	1.30279	2.532	7.206	17.526	0	0	2.698	
0.082	1.29088	2.707	6.986	17.601	0	0	2.479	
0.067	1.315	2.855	7.296	17.718	0	0	2.145	

Depending on the format of your raw microprobe data, normally you can just copy and paste your data directly into your normalization spreadsheet (this saves a lot of tedious typing and prevents typos). If the element list from the original microprobe data is in a different order, you'll have to rearrange the order of your raw data columns first. I also recommend setting up individual worksheets for each major mineral group. Once you have one worksheet all set up, it's easy to just duplicate the sheet, make any necessary adjustments to the formulas, and then it's all ready for a new set of raw data.

**3.** The next set of columns start your first calculations. Here, you'll convert all your raw weight% values into raw moles. It's useful to have the atomic weights of all the elements as a separate set of cells, to make the calculation set-up easier. See example:

corrected raw weight percent converted to raw moles									
F	Na	Mg	Al	Si	P	S	Cl	K	
18.9984	22.9898	24.305	26.9815	28.0855	30.9738	32.06	35.453	39.0	
0.00747	0.08712	0.30677	0.26926	0.6727	0.00052	0.00075	0.00087	0.041	
0.00816	0.01657	0.44649	0.05359	0.90559	0	0	0.00178	0.001	
0.00537	0.00696	0.39082	0.0245	0.90869	0	0.00047	0.00039	0.001	
0.00463	0.00595	0.39605	0.02946	0.89548	0	0.00265	0.00068		
0.01469	0.00839	0.38469	0.02691	0.9193	0	0	0.00276	0.001	
0.005	0.01739	0.40868	0.04499	0.9067	0	0	0.00172	0.001	
0.00337	0.05667	0.10418	0.26707	0.62402	0	0	0.0761	0.031	

Note that the first row of numbers, in **bold** font, is the atomic weights of the listed elements.

The general formula for calculating the raw moles is:

$$\text{weight\% of element} / \text{atomic weight of element} = \text{raw moles of element}$$

In Excel notation, a representative formula (typed into cell Z23, for example):

$$=M23/Z\$4 \quad (\text{where M23 is the cell containing the weight\% of some element})$$

For the atomic weight reference, notice the \$ sign for the cell row. The \$ sign insures that when you copy the formula down, it always references the atomic weight row.

4. In the next two columns (labeled "normalization scheme" and "ideal cation sum", respectively), you should identify the normalization scheme you plan to use, and the ideal cation sum (the integer value the normalizing elements should add up to; see below). This first column really just serves as a "comment" to remind you what you're going to be doing... the actual formulas come in the next columns.

<b>DQ</b>	<b>DR</b>	<b>DS</b>	<b>DT</b>	<b>DU</b>	<b>DV</b>	<b>DV</b>
	normalization routine	normalization scheme	ideal cation sum	actual cation sum	N.F.	
	pyroxene1	$\Sigma(T+M)=4$	4	1.4810179	2.700845	
	pyroxene1	$\Sigma(T+M)=4$	4	1.6134415	2.479173	
	pyroxene1	$\Sigma(T+M)=4$	4	1.7467446	2.289974	
	pyroxene1	$\Sigma(T+M)=4$	4	1.7509	2.284539	
	spinel	$\Sigma(T+M)=3$	3	1.8161827	1.651816	
	olivine	$\Sigma(T+M)=3$	3	1.9878379	1.509177	
	olivine	$\Sigma(T+M)=3$	3	2.0139174	1.489634	
	olivine	$\Sigma(T+M)=3$	3	1.9052297	1.574613	
	olivine	$\Sigma(T+M)=3$	3	1.8986423	1.580076	
	pyroxene1	$\Sigma(T+M)=4$	4	1.8842993	2.122805	
	pyroxene1	$\Sigma(T+M)=4$	4	1.7472433	2.289321	

There are hundreds (if not more) possible normalization schemes. A few important examples are given below:

Simple non-defect (i.e. no vacancies) sulfides, sulfosalts, halides and other simple minerals, where you measure every element:

galena, sphalerite:	$\Sigma(\text{all elements}) = 2$
pyrite, arsenopyrite, fluorite	$\Sigma(\text{all elements}) = 3$
chalcopyrite	$\Sigma(\text{all elements}) = 4$

In minerals where there are vacancies (i.e. pyrrhotite), you can't include any elements from the site where the vacancies occur, because you don't know how many atoms of those elements are supposed to be present. Hence:

pyrrhotite:	$\Sigma(\text{all elements in S site only}) = 1$
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Most minerals you'll normalize, such as silicates, carbonates, sulfates, etc., contain oxygen, which is not normally measured by electron microprobe. There are two main categories of normalizations for these minerals.

- In the first category, minerals can be normalized to the number of theoretical oxygens (or "oxygen equivalents", if OH is present).
- In the second category, minerals can be normalized to some or all of the cations present. Because of the "some or all", there may be alternative cation-based normalization schemes for a single mineral.

Sometimes the first method is better, and sometimes the second method is better. Sometimes only one method will give realistic results. In general, I prefer the second method (normalizing to cations) and I'll emphasize cation-based techniques in these instructions. Here is a summary of typical normalization schemes for minerals you'll likely encounter. Note that some of these are relatively simplified, and might need to be adjusted if you have extremely unusual compositions. The major mineralogical journals (American Mineralogist; the Canadian Mineralogist; European Journal of Mineralogy; among others) periodically publish papers reviewing and updating the nomenclature of important or complex mineral groups; these can be great resources to find suggestions for the best normalization routines to use.

hematite:	$\Sigma(\text{VI}M) = 2$
	or alternatively: oxygen = 3; (assign $\text{Fe}^{3+}/\Sigma\text{Fe} = 1$ )
ilmenite	$\Sigma(\text{VI}M) = 2$
rutile	$\Sigma(\text{VI}M) = 1$
spinel group minerals	$\Sigma(\text{T} + \text{VI}M) = 3$
calcite and aragonite group minerals	$\Sigma(\text{VI}M) = 1$
dolomite, ankerite	$\Sigma(\text{VI}M) = 2$
barite, anhydrite, monazite	$\Sigma(\text{T} + \text{IX-X}A) = 2$
apatite	$\Sigma(\text{T} + \text{"Ca site"}) = 8$

olivine group minerals	$\sum(T+^{VI}M) = 3$
	or alternatively: oxygen = 4; (assign value for $Fe^{3+}/\sum Fe$ )
zircon, xenotime	$\sum(T+^{VIII}M) = 2$
titanite	$\sum(T+^{VI}M+^{VII}M) = 3$
garnet	$\sum(T+^{VI}M+^{VIII}M) = 8$
kyanite, andalusite, sillimanite, topaz	$\sum(T+"Al\ site") = 3$
epidote, clinozoisite	$\sum(T+^{VI}M+"Ca\ site") = 8$
	or alternatively: oxygen = 12.5; (assign value for $Fe^{3+}/\sum Fe$ )
allanite	$\sum(T+^{VI}M+"Ca\ site") = 8$
beryl	$\sum("Si\ site"+"Al\ site") = 8$
	or alternatively: $\sum(T+^{VI}M) = 11$ , if Be is reliably measured
cordierite	$\sum(T+^{VI}M) = 11$
tourmaline	$\sum(T+^{VI}M) = 15$
	or alternatively: $\sum(Trig+T+^{VI}M) = 18$ , if B is reliably measured
	(note that the added complications of possible Li and vacancies can make tourmaline very challenging to normalize well).
pyroxenes, wollastonite, rhodonite	$\sum(T+M1+M2) = 4$
amphiboles	$\sum(T) = 8$ (all Al in $^{VI}M$ )
	$\sum(T) = 8$ (all Al in T)
	$\sum(T+^{VI}M) = 13$ (all Fe, Mg, Mn in $^{VI}M$ )
	$\sum(T+^{VI}M+^{VIII}M) = 15$ (all Na in "A")
	$\sum(T+^{VI}M+^{VIII}M) = 15$ (all Na in $^{VIII}M$ )
	$\sum(T+^{VI}M+^{VIII}M+A) = 16$ (no vacancies)
	or alternatively: oxygen = 23; (assign value for $Fe^{3+}/\sum Fe$ )
mica, talc, pyrophyllite	oxygen = 11; assign value for $Fe^{3+}/\sum Fe$ )
chlorite, serpentine, kaolinite	oxygen = 14; (assign value for $Fe^{3+}/\sum Fe$ );
quartz	$\sum(T) = 1$
feldspar	$\sum(T) = 4$
scapolite	$\sum(T) = 12$

5. Here comes the meat of the calculation. If you are using one of the cation-based normalization methods, then in the next column (labeled "actual cation sum"), add up the *calculated raw moles* of all the elements that satisfy the requirements of your scheme. If you are normalizing to an oxygen equivalent, you can leave the "ideal cation sum" and "actual cation sum" columns blank.

Look over these examples carefully, because an error here will carry through all of the remaining calculations and result in a poor normalization.

For example:

a. if you are normalizing sphalerite, and the scheme stipulates  $\sum(\text{all elements})$ , you would add up the raw *moles* of Zn, Fe, Mn, Cd, S, Se and any other elements you have data for... nothing is excluded.

b. if you are normalizing olivine, and the scheme stipulates  $\sum(T+{}^{\text{VI}}\text{M})$ , you would add up the raw *moles* of Si, Al, Mg, Fe, Ni and any other elements that would occur in the T and  ${}^{\text{VI}}\text{M}$  sites. If you have tiny amounts of elements like Na and K, which don't have a normal site in olivine, it's usually safest to exclude them. In most cases, if you have large amounts of an element you're not supposed to have (i.e. you have an "olivine" that has several weight% K), you've probably misidentified the mineral.

c. if you are normalizing amphibole, and the scheme stipulates  $\sum(T+{}^{\text{VI}}\text{M}+{}^{\text{VIII}}\text{M})$ , but further limits that all Na must be in "A", you would add up the raw *moles* of Si, Al, Mg, Fe, Ca and any other elements that would normally occupy the T,  ${}^{\text{VI}}\text{M}$  and  ${}^{\text{VIII}}\text{M}$  sites. However, you would *not* include Na (even though Na does occur in the  ${}^{\text{VIII}}\text{M}$  site in some amphiboles... here the rule stipulates that there can be no Na in the  ${}^{\text{VIII}}\text{M}$  site). Likewise, you would *not* include K, F, Cl because these elements *never* occupy the T,  ${}^{\text{VI}}\text{M}$  or  ${}^{\text{VIII}}\text{M}$  sites. Note that if your assumption of no Na in the  ${}^{\text{VIII}}\text{M}$  site is not appropriate, your normalization will be poor, and you'll need to try a different normalization scheme (for example, one that stipulates that all Na must be in  ${}^{\text{VIII}}\text{M}$ , or alternatively, one which allows Na to be distributed across both sites).

d. if you are normalizing feldspar, and the scheme stipulates  $\sum(\text{T})$ , you would add up the raw *moles* of Si, Al, Fe (ultimately as  $\text{Fe}^{3+}$ , since there is no other site for  $\text{Fe}^{2+}$ ) and any other elements that would normally occupy the T site. However, you would *not* include Na, K or Ca, since these elements *never* occupy the T site. You might consider it odd to not simply include Na, K and Ca, and then normalize the feldspar formula to a scheme  $\sum(\text{T}+\text{A})$ , since there are nominally no vacancies in the A site in feldspars. This convention, however, is due to an analytical artifact: the electron beam can sometimes induce alkali migration in some minerals, mimicking vacancies. Normalizing to  $\sum(\text{T})$  doesn't prevent this problem, but it does tend to yield more reasonable results.

e. normalizing sheet silicates using the cation normalization method is complex and involves iteratively estimating the  ${}^{\text{VI}}\text{M}$  site vacancies until a satisfactory normalization is produced (optimizing site fillings, charge balance, and analytical total). Note that the "ideal cation sum" will not necessarily be an integer in this case, but likely a decimal number close to either the upper or lower numerical range (closer to the upper value if the mineral is mostly trioctahedral, and closer to the lower value if the mineral is mostly dioctahedral [values in the middle are unusual]).

For beginning students, it is generally simpler to normalize sheet silicates to an oxygen equivalent (even though trying the cation method is a great exercise, and mastery of it will make you the expert on mineral normalizations!) The oxygen equivalent method is described in more detail below.

**6. The next column should be labeled "normalization factor", or simply "N.F."**  
This N.F. is important, and will be used repeatedly in further calculations.

The general formula for cation-based normalizations is:

$$\text{N.F.} = (\text{ideal cation sum}) / (\text{actual cation sum})$$

In Excel notation, the formula (typed into cell DV23, for example) is:

$$=\text{DT23}/\text{DU23}$$

The general formula for oxygen-equivalent based normalizations is:

**N.F.** = (sum of the negative charge) /  $\Sigma(\text{raw moles cation} * \text{charge})$ , where

$\Sigma(\text{raw moles cation} * \text{charge})$  means:

(raw moles Na + K) \* (+1) + (raw moles Mg + Fe<sup>2+</sup> + Ca + Mn + etc.) \* (+2) + etc.

F and Cl are not included in the cation sum, but should be included in the negative charge calculation (see below how this works). Notice that you also have to make an assumption about the relative amounts of Fe<sup>2+</sup> and Fe<sup>3+</sup>.

7. The next six columns deal with charge balance. This section can be a little confusing, so we'll walk through each column one by one. This section also introduces our first use of "IF" statements in MS Excel formulas.

EA	EB	EC	ED	EE	EF	EG	EH
	$\Sigma(-)$	$\Sigma(+)$ w/o Fe	$\Sigma(+)$	charge balance	normalized Fe3+	Fe3+/ $\Sigma$ Fe	
	-12	11.61739	12	0	0.103295	0.739618	
	-12	10.6136	12	0	0.003972	0.005746	
	-11.9945	10.6524	11.9992	0.004739	0	0	
	-12	10.55504	12	0	0.034497	0.048915	
	-12	10.60721	12	0	0.013049	0.018915	
	-11.9905	10.65145	11.99053	0	0.012826	0.019342	
	-11.9778	11.50214	12.11529	0.137449	0	0	

**A.** Column EB (labeled " $\Sigma(-)$ "). This is the sum of the negative charge. In some cases, you can determine this value just by looking at the general formula of the mineral.

Here are some examples, illustrating a few potential complications:

**a.** if you are normalizing a spinel group mineral (e.g. magnetite), you know there are 4 oxygens in the general formula. So  $\Sigma(-) = 4 * (-2) = -8$ .

**b.** if you are normalizing amphibole, you know there are 22 oxygens in the general formula, as well as 2 (OH). So  $\Sigma(-)$  would seem to be  $22 * (-2) + 2 * (-1) = -46$ . But, if your analysis includes some F and/or Cl, these halogens replace some of the OH in the formula. Fortunately, the charge of F, Cl and OH are all the same, so technically you can treat (OH+F+Cl) as simply being equivalent to "OH". In this case, the calculation doesn't change. However, in some volcanic amphiboles (notably kaersutite), some OH is

replaced by O. In this case,  $\Sigma(-)$  is no longer -46, and the calculation is much more complex (and not covered here).

c. if you are normalizing pyroxene, you know there are 6 oxygens in the general formula. So  $\Sigma(-)$  would seem to be  $6 * (-2) = -12$ . But, if your analysis includes a small amount of F or Cl, and you believe it's real, then that halogen replaces an equal *molar* amount of O (since there's no special OH site for the halogen to enter), so the net negative charge must be reduced. Here's the calculation:

As an example, let's say you originally calculated 0.00816 raw moles of F. However,  $\Sigma(-)$  is based on *normalized* moles, not raw moles (!!!!)

normalized moles F = (raw moles F) \* N.F.

so:  $0.00816 * 2.3456 = 0.01914$  (in this example, the 2.3456 is just a hypothetical number, but you can see it's comparable to the other N.F. values for pyroxene in one of the previous illustrations). Now, the overall negative charge can be calculated:

$$\Sigma(-) = (6 - 0.01914) * (-2) + (0.01914) * (-1) = -11.9809$$

The first term is the actual amount of O (reduced by a small amount of F) times its charge, added to the small amount of F times its charge.

d. Some elements on the right side of the periodic table can be a little ambiguous, so be careful. S in a sulfide would be treated as a negative species (-2 in general), but S in feldspar (presumably replacing Si) would be treated as a cation (+6), as would S in barite. S in scapolite is also probably (+6), but in this case it doesn't replace Si, but rather occurs as discrete  $\text{SO}_4^{2-}$  ions in the large cavities. In this case, the sulfate ion would be considered as contributing to the overall negative charge of the mineral. This is not an issue with most elements.

**B.** Column EC (labeled " $\Sigma(+)$  w/o Fe"). This is the sum of the positive charge, excluding Fe. This is a fairly straightforward calculation. The only trick is remembering that *normalized* moles need to be used in this calculation, *not* raw moles. So raw moles are converted to normalized moles by multiplying by the N.F.

Here's the calculation:

$$\text{N.F.} * [(\text{raw moles Na} + \text{K}) * (+1) + (\text{raw moles Mg} + \text{Ca} + \text{Mn} + \dots) * (+2) + \text{etc.}]$$

**C.** We skip ahead to column EF (labeled "normalized  $\text{Fe}^{3+}$ "). Although the formula looks a little complicated, it can be readily derived with a bit of algebra. Keep in mind that this is a *computational* estimate of  $\text{Fe}^{3+}$ . Calculated  $\text{Fe}^{3+}/\Sigma\text{Fe}$  could differ markedly from the true value, simply because by default, the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  calculation incorporates all of the cumulative analytical uncertainty.

Here's the basic calculation:

$$\text{normalized Fe}^{3+} = -(\Sigma(-) + (\Sigma(+)\text{ w/o Fe})) - 2 * \text{N.F.} * (\text{raw moles total Fe})$$

In Excel notation, the formula (typed into cell EF23, for example) is:

$$=-(EB23 + EC23) - 2 * DV\$23 * CU23 \text{ (where CU23 represents raw moles total Fe)}$$

The only complication that can occur is that if the analysis isn't that great (or total Fe in the mineral happens to be very low), the Fe<sup>3+</sup> calculation can occasionally yield a negative number, or alternatively, a value for Fe<sup>3+</sup> greater than the total Fe present in the sample. Clearly neither of these potential outcomes is acceptable.

Here is where "IF" statements are added to the formula, to ensure that if the calculation yields a negative number, the result is replaced by zero, and if the calculation alternatively yields a result greater than total Fe, that result is replaced by total normalized Fe. Note that the nested "IF" statement accommodates both possibilities.

In Excel notation, building on the previous example, the formula would be:

$$=IF((- (EB23 + EC23) - 2 * DV\$23 * CU23) < 0, 0, IF((- (EB23 + EC23) - 2 * DV\$23 * CU23) > DV\$23 * CU23, DV\$23 * CU23, - (EB23 + EC23) - 2 * DV\$23 * CU23))$$

**D.** Continue with column EG (labeled "Fe<sup>3+</sup>/ΣFe").

Here's the basic calculation:

$$\text{Fe}^{3+}/\Sigma\text{Fe} = (\text{normalized moles Fe}^{3+}) / \text{N.F.} * (\text{raw moles total Fe})$$

In Excel notation, building on the previous example, the formula would be:

$$=EF23/(DV\$23 * CU23)$$

Note that this value is a mole ratio and has to be between 0 and 1.

**E.** Returning to column ED (labeled "Σ(+)").

Here's the basic calculation:

$$\Sigma(+) = (\Sigma(+) \text{ w/o Fe}) + (\text{normalized moles Fe}^{3+}) * (+3) + (\text{normalized moles Fe}^{2+}) * (+2)$$

In Excel notation, building on the previous example, the formula would be:

$$=EC23 + EF23 * 3 + (DV\$23 * CU23) * (1 - EG23) * 2$$

**F.** Concluding with column EE (labeled "charge balance"). This is a simple calculation.

Here's the basic calculation:

$$\text{charge balance} = \Sigma(+) + \Sigma(-)$$

In Excel notation, building on the previous example, the formula would be:

=EB23 + ED23

Ideally, the charge balance should be zero. If the result is far from zero (in either direction, + or -), either the normalization scheme is not the right one, or the analysis is not of high quality. Remember, even if the result is zero, that's not a guarantee that the normalization scheme is correct, or that the analysis is necessarily of high quality. This may be especially true in silicates with high amounts of Fe; a seemingly plausible (but totally incorrect)  $\text{Fe}^{3+}/\sum\text{Fe}$  might hide a poor quality analysis. Also, using an oxygen equivalent normalization scheme forces a charge balance, so definitely in this case, apparent charge balance provides no assurance of a high quality analysis.

8. Now comes the fun part... filling the various structural sites. We generally start with the smallest site (usually the tetrahedral site) and work our way up to the largest cation site, and finally finish with the OH site (if present). For minerals like scapolite or feldspathoids, additional calculations involving  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and/or  $\text{S}^{2-}$  may be necessary. Elements that can occur in multiple sites (like Al, see below) must be appropriately divided up. The following illustration shows part of the cation filling scheme for titanite. We'll develop in greater detail how these values are calculated.

EI	EJ	EK	EL	EM	EN	EO	EP	EQ	ER	ES	ET
	normalized moles with site assignments										
	(T) Si	(T) Ge	(T) P	(T) S	(T) Al	$\sum(\text{T})$		(VI) Ti	(VI) Al	(VI) Fe3+	(VI) Fe2+
	0.99	0.00	0.00	0.00	0.01	1.00		0.89	0.04	0.06	0.01
	0.97	0.00	0.00	0.00	0.03	1.00		0.92	0.01	0.05	0.01
	0.98	0.00	0.00	0.00	0.02	1.00		0.90	0.02	0.07	0.01
	0.97	0.00	0.00	0.00	0.03	1.00		0.93	0.02	0.03	0.01
	0.98	0.00	0.00	0.00	0.01	1.00		0.91	0.04	0.03	0.01
	0.98	0.00	0.00	0.00	0.02	1.00		0.94	0.01	0.02	0.01

**A.** Elements that occur in only one site (such as Si) are the easiest to calculate. Again, remember that we use *normalized* moles here.

Here's the calculation:

normalized moles Si = N.F. \* (raw moles Si)

This calculation is repeated for each T site element until you get to Al.

**B.** Unless the normalization scheme specifically does not allow Al in the T site (one amphibole normalization has this constraint, so be aware), the remaining available space in the T site can be filled with Al.

Here's the calculation:

$${}^{\text{IV}}\text{Al} = (\text{total T}) - (\sum(\text{all other T site cations}))$$

Despite its apparent simplicity, sometimes this calculation fails. If the quantity " $\sum(\text{all other T site cations})$ " already exceeds the maximum allowable site filling even without Al, the  ${}^{\text{IV}}\text{Al}$  calculation will clearly produce a negative number. Similarly, if the calculated  ${}^{\text{IV}}\text{Al}$  exceeds the actual total amount of Al present, then this value is meaningless, and a negative number will result for  ${}^{\text{VI}}\text{Al}$  when you start the  ${}^{\text{VI}}\text{M}$  site fillings. A nested "IF" equation similar to the one used in the  $\text{Fe}^{3+}$  calculation avoids this potential pitfall.

In Excel notation, the formula (typed into cell EN23, for example) would be:

$$=\text{IF}(\text{SUM}(\text{EJ23:EM23})>1,0,\text{IF}(1-\text{SUM}(\text{EJ23:EM23})>\text{DV}\$23 * \text{CP23},\text{DV}\$23 * \text{CP23},1-\text{SUM}(\text{EJ23:EM23}))$$

**C.** When you start on the next set of site fillings (in this example,  ${}^{\text{VI}}\text{M}$ ), start with Al. Nominally, if your previous "IF" statement works correctly, the calculation is fairly straightforward:

$${}^{\text{VI}}\text{Al} = (\text{total normalized moles Al}) - (\text{normalized moles Al in T})$$

In Excel notation, the formula (typed into cell ER23, for example) would be:

$$=(\text{DV}\$23 * \text{CP23}) - \text{EN23}$$

**D.** These same three steps (A, B, and C) are used to progressively fill all the cation sites in the mineral. In addition to Al, be aware of other elements that can occur in multiple cation sites (such as Na, which may occur in two sites in amphibole, and  $[\text{Fe}+\text{Mg}+\text{Mn}]$ , which may occur in multiple sites in a number of minerals). Depending on what mineral you're normalizing (and the rules associated with the normalization scheme you're using), you'll need to treat these elements in a way analogous to Al in the previous example.

**E.** Dealing with cation site vacancies:

Many minerals have cation site vacancies. Here are some examples:

- a. the "Fe" site in pyrrhotite:  $\text{Fe}_{1-x}\text{S}$
- b. the A site in amphiboles
- c. the  $\text{VI}$ M site in chlorites, kaolinite and pyrophyllite
- d. the A and  $\text{VI}$ M sites in micas

For the most part, vacancies are treated just like any cation during site filling. For minerals with vacancies, be sure to include an extra column in your spreadsheet for each site that a vacancy may occur at. Vacancies are calculated by difference:

$$\text{vacancies} = (\text{total allowable filling of site}) - (\text{actual filling of site})$$

You'll want to include an "IF" statement to ensure that vacancies are not allowed to be a negative number.

#### F. Calculating normalized moles of OH:

You'll notice for hydrous minerals, your microprobe analytical totals will be significantly less than 100%. The missing mass is probably mostly  $\text{H}_2\text{O}$ , which the microprobe cannot analyze for (although there are several other reasons for low totals as well: significant  $\text{Fe}^{3+}$  [e.g. in hematite, magnetite, epidote], elements like Li that cannot be analyzed by electron microprobe [e.g. in spodumene, petalite], other elements which are present but that you didn't analyze for, beam overlap on multiple phases, or simply a bad analysis). Barring these additional considerations, for many (but not all) hydrous minerals, it is often possible to estimate the  $\text{H}_2\text{O}$  content based on your normalization. Like the  $\text{Fe}^{3+}/\sum\text{Fe}$  calculation, however, the accuracy of your estimate is significantly dependent on the quality of your analysis.

After setting up and filling all of your cation columns, you should set up three additional columns for an "OH" site (one column each for F, Cl, and OH), assuming the mineral has an "OH" site that can accommodate these elements. For a mineral such as pyroxene, which doesn't have an "OH" site, it is sufficient to just set up two columns for any observed F or Cl. For a mineral like titanite, which has a mixed (O,OH) site, you should add a fourth column for extra O.

The simplest calculation of OH is by difference, similar to how cation vacancies were calculated previously:

$$\text{normalized moles OH} = (\text{total allowable filling of "OH" site}) - (\text{normalized moles F} + \text{Cl})$$

Except in rare circumstances when (F + Cl) completely fills the "OH" site, you'll rarely have to worry that calculated OH could yield an unrealistic negative value.



In Excel notation, a representative formula for K<sub>2</sub>O (typed into cell HQ23, for example) would be:

=AJ23\*HQ\$4/2 (where AJ23 is the cell containing the raw moles of K, in this example)

For the molecular weight reference, notice the \$ sign for the cell row. The \$ sign insures that when you copy the formula down, it always references the molecular weight row.

This calculation works for most of the oxides; however, certain elements have specialized calculations:

**A:** for F and Cl:

These elements don't occur as oxides, so the raw weight% values from the microprobe are copied directly into the F and Cl cells... easy, huh?

**B:** for H<sub>2</sub>O:

The calculation is:

$$\text{weight\% H}_2\text{O} = (\text{normalized moles OH}) / (\text{N.F.}) * (\text{molecular weight H}_2\text{O}) / 2$$

**C:** for FeO:

The calculation is:

$$\text{weight\% FeO} = (\text{total normalized moles Fe}^{2+}) / (\text{N.F.}) * (\text{molecular weight FeO})$$

**D:** for Fe<sub>2</sub>O<sub>3</sub>:

The calculation is:

$$\text{weight\% Fe}_2\text{O}_3 = (\text{total normalized moles Fe}^{3+}) / (\text{N.F.}) * (\text{molecular weight Fe}_2\text{O}_3) / 2$$

Following the oxide columns, there are three remaining columns: one column labeled "subtotal", followed by a column labeled "O=(F+Cl)", and concluding with a column labeled "total". The "sub-total" column sums all the oxides (+F + Cl). The "O=(F+Cl)" column corrects for excess oxygen (since some of the assumed metal "oxides" are must actually be metal "fluorides" or "chlorides"... the F and Cl are bonded to the cations).

The calculation is:

$$\text{O}=(\text{F}+\text{Cl}) = - (\text{wt\% F} * (16/38) + \text{wt\% Cl} * (16/70.91))$$

Note that this value is a negative number.

The "total" column sums the "sub-total" column and the "O=(F+Cl)" column.

**10.** Congratulations, you're done. Woo hoo!

**Appendix.** The spreadsheet is complete, but for publication purposes (i.e. your thesis or a manuscript), you'll need to name your mineral, and have one or more formatted tables of analytical data. For many simple minerals like chalcopyrite or fluorite, the naming is easy. But for more typical solid solutions (most minerals), you'll need to use your calculated site fillings and possibly some published nomenclature rules to name your mineral.

As for presenting your analytical data as formatted tables, see the following illustration. Open any mineralogy journal and you'll find countless other examples:

TABLE 4. RECOMMENDED NORMALIZATIONS OF K-DOMINANT AMPHIBOLES

DHZ	13-33	14-25	14-57	15-20	15-22	15-31	15-39	15-40	15-41	16-1
Si <i>apfu</i>	6.67	6.06	6.13	5.75	6.12	5.72	6.05	6.02	5.67	4.61
<sup>IV</sup> Al	1.33	1.94	1.87	2.25	1.85	2.28	1.95	1.98	2.33	3.39
$\Sigma(T)$	8.00	8.00	8.00	8.00	8.00(c)	8.00	8.00	8.00	8.00	8.00
<sup>VI</sup> Al	0.15	0.78	0.54	0.33	0.19	0.02	0.35	0.60	0.62	1.08
Fe <sup>3+</sup>	0.22		0.38	1.23	0.60	1.04	0.41	0.19	0.29	0.34
Fe <sup>2+</sup>	4.29	1.07	3.47	2.29	3.20	3.34	3.84	2.01	2.03	1.60
Mg	0.14	3.06	0.55	0.96	0.92	0.46	0.10	2.05	1.84	1.50
Mn <sup>2+</sup>	0.19	0.00	0.03		0.06		0.22	0.02	0.02	0.01
Ti	0.01	0.09	0.03	0.17	0.04	0.13	0.08	0.12	0.19	0.46
Cr				0.02						
$\Sigma(M1, M2, M3)$	5.00	5.00	5.00	5.00	5.00	4.98	5.00	5.00	5.00	5.00
xM <sup>2+</sup>		0.03 Fe 0.01 Mn		0.28 Fe			0.04 Mn 0.03 Mn			
Ca	2.00	1.96	1.91	1.53	1.96	2.00	1.96	1.97	2.00	2.00
Na			0.09	0.19	0.04					
$\Sigma(M4)$	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Na	0.18	0.40	0.22	0.01	0.37	0.24	0.49	0.28	0.06	0.30
K	0.63	0.48	0.76	0.51	0.61	0.72	0.55	0.60	0.90	0.72
$\Sigma(A)$	0.87(a)	0.93(b)	0.98	0.52	0.99	0.98(d)	1.03	0.92(e)	1.00(f)	1.03(g)
OH	0.46	1.81	0.84	0.35		0.58	1.84	1.88	1.88	2.00
F	0.18	0.07		0.51				0.10	0.11	
Cl	1.37	0.11	1.16	1.14	2.08	1.42	0.16	0.03	0.01	
optimized Fe <sup>2+</sup> / $\Sigma$ Fe	0.048	0.000	0.099	0.324	0.158	0.238	0.096	0.088	0.124	0.175
name*	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)

a substantial literature characterizing potassium-rich amphiboles, a limited number of potassium-dominant amphiboles have only recently (since 1997) been conferred species status. This represents an unfortunate and surprisingly enigmatic situation, especially in light of

(Na,K), whereas the CNMMN list of approved minerals gives it as (K,Na) (Nickel & Nichols 2002). Matsubara *et al.* (2002) observed: "It should be remarked that kornite has a higher K content (0.64 *apfu*) than potassicleakeite. This suggests that the name be

Hopefully this guide will help you get the most out of your microprobe analytical experience. With all the formulas contained herein, it's possible there could be an inadvertent typo or two. If anything seems off or just isn't working, let me know and I'll work to improve it in a future addition. Happy and successful analyzing!