Term: Fall 2018 **Course: GEOL 311**

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Lab 5 – Calculation of mineral's formula from chemical analyses

Think of enstatite, a magnesium end-member of orthopyroxene group. Its formula expressed in the conventional way looks like this - $Mg[SiO_3]$. The square brackets are used to emphasize the building block of chain silicates. The chemical content of enstatite also can be expressed in neutrally-charged molecules of oxides according to the proportions of cations and oxygens in the mineral – $MgO \cdot SiO_2$ (1:1). Another example: $2MgO \cdot SiO_2$ would make up mineral forsterite (olivine group) with formula $Mg_2[SiO_4]$. This form of mineral formula was used in early days of mineralogy, when mineral structures were not deciphered completely and it was assumed that all atoms of metals are bonded with oxygen. Even though now we use chemical and structural basis to identify minerals, the results of chemical analyses are still reported in per cents of oxides by weight. There are two main reasons why it is done that way: 1) we do not analyze oxygen directly and 2) we assume that the negatively-charged oxygen cancels out the positive charge of cation, making minerals neutrally-charged.

So, if you send a sample of enstatite to a chemical laboratory the result will come back in form

oxide	Weight % (wt. %)
SiO_2	59.85
MgO	40.15
Total	100

Note, that it is not just 50 wt. % and 50 wt. % of SiO_2 and MgO, even though enstatite is $MgO \cdot SiO_2$ (1:1). The oxides have different molecular weights: magnesium oxide is ~20 atomic units lighter than silicon dioxide. Accounting for that you can recalculate formula in a way:

oxide	wt. %	Molecular weight (from periodic table)	Molecular ratio (x10000)	Cation ratio	Oxygen ratio
SiO_2	59.85	*60.084*	=10000x(59.85/60.084)=9961	1 silicon atom = 9961	Two oxygen atoms= 19922
MgO	40.15	*40.304*	=10000x(40.15/40.304)=9961	1 magnesium = 9961	9961
Total	100				

Now you see that the proportion of SiO_2 to MgO molecules, is 1:1 (as well as Si:Mg). However, to write the formula you need to find a normalization factor.

The general instructions are:

1. Find molecular proportion of each oxide by dividing wt. % by molecular weight (we just did). Multiplication by 10000 is done for convenience, so that we can round up the numbers and get rid of the decimal point.
2. Simply multiply molecular ratios by amount of cations and oxygens in each oxide and write it down in corresponding columns. To get cation ratio for Si, the molecular ratio of SiO_2 was multiplied by 1 because SiO_2 has one atom of Si. Since SiO_2 has 2 atoms of O, oxygen ratio was calculated by multiplying the molecular ratio of SiO_2 by 2.
3. The amount of oxygen in the mineral is governed by the stoichiometry. In other words, knowing that there will be 3 atoms of oxygen total in the formula (see SiO_2 + MgO), you need to calculate a normalization factor from total the total of oxygen in formula and then divide that number by 3. In our case, take total proportion of oxygen and divide it by three.
4. Divide every cation ratio by the normalization factor. The resulted numbers are atoms per formula units (apfu).

oxide	wt. %	Molecular weight	Molecular ratio (x10000)	Cation ratio	Oxygen ratio	Atoms per formula units
SiO_2	59.85	*60.084*	9961	9961	19922	Si: =9961/9961=1.00
MgO	40.15	*40.304*	9961	9961	9961	Mg: =9961/9961=1.00
Total	100				TOTAL = 29884; 3012/3=9961 (normalization factor!)	

The finalized formula is $Mg_{1.00}[Si_{1.00}O_3]$.

Now try to write a formula of this mineral:

Sample A1

Oxide	wt. %	Molecular weight	Molecular ratio	Cation ratio	Oxygen ratio	a.p.f.u.	Charge check
SiO_2	28.29	*60.084*					
ZrO_2	38.68						
HfO_2	33.03						
Total	100.00						

Remember to look at the actual mineral (sample sitting at the table). Identifying it will help you to solve the formula (to get the amount of oxygen per formula). Also, looking at elements that compose the mineral might help (especially in the analysis above). You also should keep in mind that nothing is perfectly pure and isomorphic substitution will result in deviation from a formula of a theoretical endmember.

Here is another fun example. See the mineral specimen at the front desk. Identify the mineral and provide your answer with all the diagnostic features (habit, appearance, color, hardness, fracture, cleavage, etc., i.e. everything). It is encouraged to use full sentences. Make sure you identify the mineral correctly. See your TA if you are uncertain in the mineral identification. This analyses were obtained from real minerals and thus, the compositions are deviated from theoretical endmembers even more. The final answer should be written in stoichiometric form with indices rounded to the second digit after decimal, e.g. monazite:

$$(Ce_{0.55}\,La_{0.40}\,Nd_{0.04}\,Th_{0.01})_{1.00}[(P_{0.99}\,Si_{0.01})_{1.00}O_4].$$

Use your understanding of charge and size of ions to see where you would incorporate elements that do not form an endmember. For example Na, K and Ca are commonly substituting each other in feldspars. In addition, Rb^+, Cs^+ and Li^+ may find themselves comfortable among those atoms within the same structure. Check charges. Use the space below for calculations and identification. Feel free to attach an additional sheet of paper if you need. The analysis is reported in weight per cents.

SiO_2	52.23
Al_2O_3	2.27
Fe_2O_3	0.95
MgO	16.45
FeO	2.53
CaO	25.57
Total	100