Lecture Notes - Mineralogy - Calculating Mineral Formulas

Diopside Analysis	
SiO_2	**55.49**
MgO	**18.61**
CaO	**25.90**
Total	**100.00**

- Chemical analyses for minerals are commonly reported in **mass units**, usually weight percentages of the oxides of the elements determined. Although little weighing is involved in most modern chemical analyses, **weight percentages** are reported for historic reasons (chemists performed their analyses using gravimetric techniques). Analyses are given in terms of **oxides** of the elements, although oxygen is normally not determined. It is assumed that each mineral is electrically neutral and that the positive charges on the cations are balanced by an appropriate quantity of oxygen anions. Unfortunately, mass units are not the most convenient units for many problems. They obscure relationships that are obvious when the compositions of minerals are expressed in terms of atomic proportions.

- The datum for each element in an analysis is in units of:

$$\text{weight \% of oxide of element} = \frac{\text{grams of oxide of element}}{\text{hectogram of mineral}}$$

The desired mineral formula is in units of:

$$\frac{\text{atoms of element}}{\text{formula of mineral}} = \frac{\text{moles of element}}{\text{mole of mineral formula}}$$

Retrieval of standard chemical formulas for minerals from chemical analyses is an exercise in (a) conversion of units of quantity and (b) normalization of sums. Conversion of one unit of quantity to another is straightforward if the unit of quantity for each number is written out in the calculation. Normalization is simply multiplying all terms in the analysis by a constant, thereby changing the sum while preserving the relative proportions. The following is a general procedure, illustrated for the ideal diopside analysis listed above.

Step #1 - Divide the weight percentage of each oxide by the formula weight of that oxide.

$$\frac{\text{weight \% of SiO}_2}{\text{formula weight of SiO}_2} = \frac{\dfrac{\text{grams of SiO}_2}{\text{hectogram of mineral}}}{\dfrac{\text{grams of SiO}_2}{\text{mole of SiO}_2}} \qquad \frac{55.49}{60.085} = 0.92353 \qquad \frac{\text{moles of SiO}_2}{\text{hectogram of mineral}}$$

$$\frac{\text{weight \% of MgO}}{\text{formula weight of MgO}} = \frac{\dfrac{\text{grams of MgO}}{\text{hectogram of mineral}}}{\dfrac{\text{grams of MgO}}{\text{mole of MgO}}} \qquad \frac{18.61}{40.311} = 0.46166 \qquad \frac{\text{moles of MgO}}{\text{hectogram of mineral}}$$

$$\frac{\text{weight \% of CaO}}{\text{formula weight of CaO}} = \frac{\dfrac{\text{grams of CaO}}{\text{hectogram of mineral}}}{\dfrac{\text{grams of CaO}}{\text{mole of CaO}}} \qquad \frac{25.90}{56.079} = 0.46185 \qquad \frac{\text{moles of CaO}}{\text{hectogram of mineral}}$$

The resulting "mole numbers" do not appear to be particularly useful because their sum is normalized to a number of moles of oxides that has a mass of 100 grams. However, because these are mole numbers, we could immediately write a formula for diopside as follows:

$$(CaO)_{0.46185}(MgO)_{0.46166}(SiO_2)_{0.92353}$$

In spite of the many digits, it is clear that the number of moles of CaO and the number of moles of MgO are nearly identical and approximately half the number of moles of SiO_2. In this case we can see "by inspection" that multiplying this formula by the constant (1/0.46185) = (2.1652) leads to nice whole numbers:

$$(CaO)_{1.0}(MgO)_{1.0}(SiO_2)_{2.0} = Ca\,Mg\,Si_2O_6$$

Unfortunately, it is not always possible to determine the proper proportionality constant "by inspection," so another procedure must be used to normalize the formula. The standard normalization for oxygen-rich mineral formlas is in terms of a specific number of oxygen atoms per formula (=moles of oxygen atoms per mole of formula). For example, feldspar formulas are commonly normalized to contain eight oxygen atoms per formula. Clinopyroxenes are commonly normalized to six oxygen atoms per formula (=six moles of oxygen atoms per mole of clinopyroxene). To get the number of oxygens to add up to the correct number, each of the oxides must be expressed in terms of the number of moles of oxygen atoms in that oxide per 100 grams of mineral.

Step #2 - Multiply the "mole number" of each oxide by the number of oxygens in the oxide formula.

$$\left(\frac{\text{moles of SiO}_2}{\text{hectogram of mineral}}\right)\left(\frac{\text{oxygen units of SiO}_2}{\text{mole of SiO}_2}\right) \quad (0.92353)(2) = 1.84705 \quad \frac{\text{oxygen units of SiO}_2}{\text{hectogram of mineral}}$$

$$\left(\frac{\text{moles of MgO}}{\text{hectogram of mineral}}\right)\left(\frac{\text{oxygen units of MgO}}{\text{mole of MgO}}\right) \quad (0.46166)(1) = 0.46166 \quad \frac{\text{oxygen units of MgO}}{\text{hectogram of mineral}}$$

$$\left(\frac{\text{moles of CaO}}{\text{hectogram of mineral}}\right)\left(\frac{\text{oxygen units of CaO}}{\text{mole of CaO}}\right) \quad (0.46185)(1) = 0.46185 \quad \frac{\text{oxygen units of CaO}}{\text{hectogram of mineral}}$$

The sum of all the resulting "oxygen numbers" (2.7705) is the number of moles of oxygen atoms per hectogram of mineral. We want this sum to be 6.0, not 2.7705. Therefore, each oxygen number is multiplied by 2.16567 (=6/2.7705) (hectogram of mineral)/(6 oxgen units of mineral)

Step #3 - Multiply the "oxygen number" of each oxide by a normalization constant (equal to the number of oxygens in the desired formula divided by the sum of the "oxygen numbers").

$$\left(\frac{\text{oxygen units of SiO}_2}{\text{hectogram of mineral}}\right)\left(\frac{\text{hectograms of mineral}}{\text{6 oxygen units of mineral}}\right) \quad (1.84705)\,(2.16567) = 4.00 \quad \frac{\text{oxygen units of SiO}_2}{\text{6 oxygen units of mineral}}$$

$$\left(\frac{\text{oxygen units of MgO}}{\text{hectogram of mineral}}\right)\left(\frac{\text{hectograms of mineral}}{\text{6 oxygen units of mineral}}\right) \quad (0.46166)\,(2.16567) = 1.00 \quad \frac{\text{oxygen units of MgO}}{\text{6 oxygen units of mineral}}$$

$$\left(\frac{\text{oxygen units of CaO}}{\text{hectogram of mineral}}\right)\left(\frac{\text{hectograms of mineral}}{\text{6 oxygen units of mineral}}\right) \quad (0.46185)\,(2.16567) = 1.00 \quad \frac{\text{oxygen units of CaO}}{\text{6 oxygen units of mineral}}$$

Finally, to get the number of atoms of each element per formula (=number of moles of each element per mole of mineral), the “normalized oxygen numbers” must be multiplied by the appropriate constants.

Step #4 - Multiply the “normalized oxygen numbers” of each oxide by the number of cations per oxygen in the oxide formula.

$$\left(\frac{\text{oxygen units of CaO}}{\text{6 oxygen units of mineral}}\right)\left(\frac{\text{moles of Ca}}{\text{oxygen unit of CaO}}\right) \quad (1.00)\,(1) = 1.00 \quad \frac{\text{moles of Ca}}{\text{6 oxygen units of mineral}}$$

$$\left(\frac{\text{oxygen units of MgO}}{\text{6 oxygen units of mineral}}\right)\left(\frac{\text{moles of Mg}}{\text{oxygen unit of MgO}}\right) \quad (1.00)\,(1) = 1.00 \quad \frac{\text{moles of Mg}}{\text{6 oxygen units of mineral}}$$

$$\left(\frac{\text{oxygen units of SiO}_2}{\text{6 oxygen units of mineral}}\right)\left(\frac{\text{moles of Si}}{\text{oxygen unit of SiO}_2}\right) \quad (4.00)\,(0.5) = 2.00 \quad \frac{\text{moles of Si}}{\text{6 oxygen units of mineral}}$$

The resulting formula $Ca\,Mg\,Si_2O_6$ was anticipated above.

- Chemical analyses obtained with an electron microprobe (wavelength dispersive) or energy dispersive x-ray spectrometer do not distinguish between the oxidation state of elements such as iron that occur in more than one valence state. For minerals that contain iron, the ferric/ferrous ratios may be estimated from microprobe analyses by normalizing according to a total number of cation per formula. For example, if there are no cation vacancies in a clinopyroxene, there will be a total of four cations per formula. In some minerals, cation vacancies and even anion vacancies are possible.

Readings

Deer, Howie, and Zussman: Appendix

Excel Spreadsheet Version of Diopside Formula Calculation

	A	B	C	D	E	F	G
1	Recalculation of a mineral formula using a fixed number of oxygens per formula						
2							
3							
4	Analysis title		**Ideal diopside**			Oxygens per	
5						formula =	
6					Oxy =	6.00000	
7							
8				**Mole**	**Oxygen**	**Normaliz.**	**Atom**
9	**Oxide**	**GFW**	**Wt.%**	**Units**	**Units**	**Ox Units**	**Units**
10							
11	SiO2	60.085	**55.49**	**0.92353**	**1.84705**	**4.00002**	**2.00**
12	TiO2	79.899		0.00000	0.00000	0.00000	0.00
13	Al2O3	101.961		0.00000	0.00000	0.00000	0.00
14	Fe2O3	159.692		0.00000	0.00000	0.00000	0.00
15	FeO	71.846		0.00000	0.00000	0.00000	0.00
16	MnO	70.937		0.00000	0.00000	0.00000	0.00
17	MgO	40.311	**18.61**	**0.46166**	**0.46166**	**0.99979**	**1.00**
18	CaO	56.079	**25.90**	**0.46185**	**0.46185**	**1.00019**	**1.00**
19	Na2O	61.979		0.00000	0.00000	0.00000	0.00
20	K2O	94.203		0.00000	0.00000	0.00000	0.00
21	H2O	18.015		0.00000	0.00000	0.00000	0.00
22							
23	**Totals**		**100.00**	**1.84703**	**2.77056**	**6.00000**	**4.00**

Excel Spreadsheet Codes for Mineral Formula Calculation

	A	B	C	D	E	F	G
4	Analysis title		**Ideal Diopside**			Oxygens per	
5						formula =	
6					Oxy =	6	
7							
8				**Mole**	**Oxygen**	**Normaliz.**	**Atom**
9	**Oxide**	**GFW**	**Wt.%**	**Units**	**Units**	**Ox Units**	**Units**
10							
11	SiO2	60.085	55.49	=C11/B11	=D11*2	=E11*Oxy/$E$23	=F11/2
12	TiO2	79.899		=C12/B12	=D12*2	=E12*Oxy/$E$23	=F12/2
13	Al2O3	101.961		=C13/B13	=D13*3	=E13*Oxy/$E$23	=F13*2/3
14	Fe2O3	159.692		=C14/B14	=D14*3	=E14*Oxy/$E$23	=F14*2/3
15	FeO	71.846		=C15/B15	=D15	=E15*Oxy/$E$23	=F15
16	MnO	70.937		=C16/B16	=D16	=E16*Oxy/$E$23	=F16
17	MgO	40.311	18.61	=C17/B17	=D17	=E17*Oxy/$E$23	=F17
18	CaO	56.079	25.9	=C18/B18	=D18	=E18*Oxy/$E$23	=F18
19	Na2O	61.979		=C19/B19	=D19	=E19*Oxy/$E$23	=F19*2
20	K2O	94.203		=C20/B20	=D20	=E20*Oxy/$E$23	=F20*2
21	H2O	18.015		=C21/B21	=D21	=E21*Oxy/$E$23	=F21*2
22							
23	**Totals**		=SUM(C11:C21)	=SUM(D11:D21)	=SUM(E11:E21)	=SUM(F11:F21)	=SUM(G11:G21)
24							
25							
26							
27			Set Oxy =	$F$6 using	(Insert/Names/	Define)	
28							