WORKING WITH ELECTRON MICROPROBE DATA FROM A HIGH PRESSURE EXPERIMENT – CALCULATING MINERAL FORMULAS, UNIT CELL CONTENT, AND GEOTHERMOMETRY

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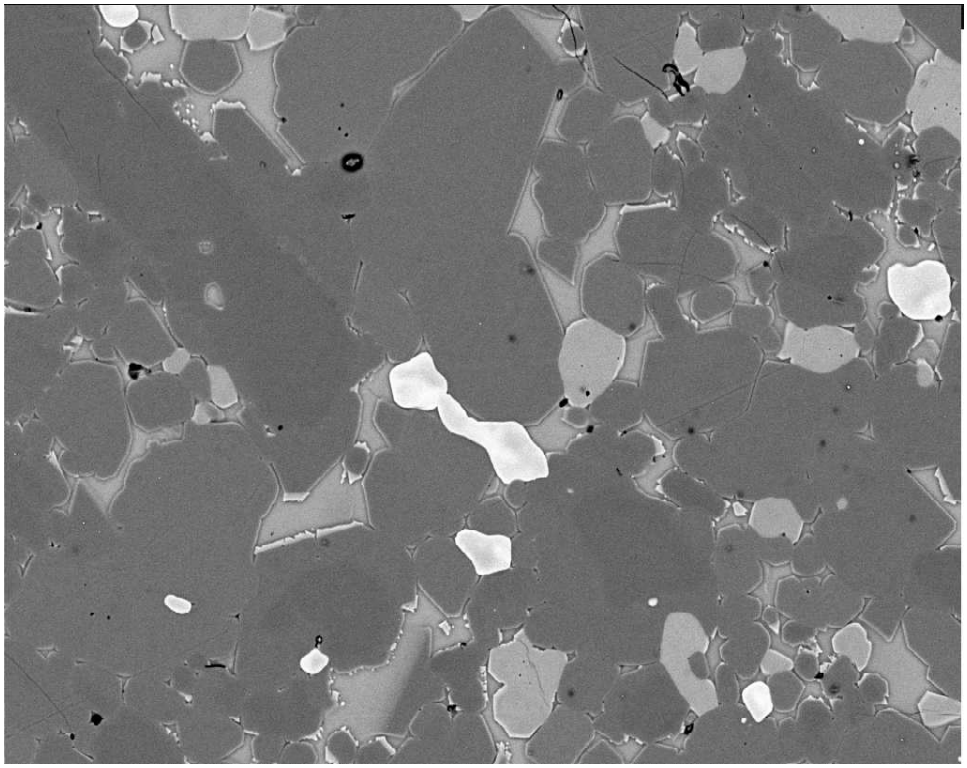


Figure 1. Back scattered electron image of peridotite partial melting experimental run product showing grains of olivine and orthopyroxene (dark gray), clinopyroxene (medium gray), spinel (white), with interstitial glass (light gray). Field of view ~200μm.

INTRODUCTION

Calculating Mineral Formula from weight percent oxide data

This exercise will introduce you to procedures commonly used to manipulate chemical data. Specifically, we will examine how chemical analyses can be recast into mineral formula and how chemical data can be combined with x-ray diffraction data to determine the atomic content of unit cells. We will also use chemical information to calculate equilibration temperature for a mantle melting experiment.

The electron microprobe (or electron probe microanalyzer, EPMA) is invaluable in producing rapid, precise analyses of a wide variety of materials in very small areas. With this instrument, individual minerals in a rock may be studied in detail. The main drawbacks of EPMA analysis include the facts that it cannot (1) accurately analyze light elements like oxygen,

nor (2) determine valence states (e.g., Fe^{2+} vs. Fe^{3+}). For this exercise we will assume that all iron is ferrous (Fe(II) or Fe^{2+}). We can, to a certain extent, get around the oxygen problem when analyzing silicate and oxide minerals, by assuming that each cation is associated with the stoichiometric amount of oxygen required to form the cation's oxide. In other words, we assume that oxide and silicate minerals are composed of mixtures of oxides, rather than individual elements. Instead of reporting an analysis as a list of weight percentages of the elements (including oxygen), we report them as weight percentages of the common oxides. Mineral formulae are then calculated from analyses assuming a fixed number of oxygen atoms in the ideal formula. This approximation is valid as long as the elements are each present in only one valence state and the mineral is truly stoichiometric. Although these are occasionally questionable assumptions, we will accept them for this exercise. Let's look at an example.

EXAMPLE:

Consider a real analysis of the mineral forsterite (Mg-olivine). The ideal, end-member formula for forsterite is Mg_2SiO_4. In nature, we typically find other divalent metal cations substituting for magnesium. One such analysis is listed below in terms of weight percentages of the oxides.

Oxide	wt.% oxide
SiO_2	40.30
FeO	8.85
MgO	49.58
CaO	0.07
MnO	0.13
NiO	0.42
Total	99.35

In order to calculate the formula for this olivine, we perform the following simple steps (modified from Deer et al., 1992 p. 678). Olivine has the general formula: $(Mg,Fe)_2SiO_4$

Step 1: Obtain the analysis (silicates are reported in terms of oxide weight percentages, which may or may not be normalized to 100%). List in column I.

Step 2: List (in column II) for each oxide the appropriate molecular weight of the oxide.

Step 3: Divide I by II to obtain the atomic proportions. Column III therefore expresses the molecular proportions of the various oxides.

Step 4: Column IV is derived from column III by multiplying by the number of oxygen atoms in the oxide concerned. It thus gives a set of numbers of oxygen atoms associated with each of the cations. At the foot of column IV is its total.

Step 5: If we require the olivine formula to be based on 4 oxygen atoms, we need to recast (normalize) the oxygen atom proportions so that they total 4. This is done by multiplying all of the oxygen proportions (col IV) by a normalization factor defined as 4/total oxygen proportions. The results of this step are given in column V.

Step 6: Column V gives the formula-normalized number of oxygen anions. We must now calculate the number of cations associated with each oxygen. Column VI is calculated by multiplying column V by the ratio of the cation to oxygen in the initial oxide. For example, in SiO_2, there is one Si for every 2 oxygens, so column $VI_{(Si)}$ is multiplied by ½. For trivalent cations such as Al_2O_3, there are 2 Al atoms for every 3

oxygens, so column V is multiplied by 2/3. For divalent cations (e.g., Ca, Mg, Fe^{2+}, etc.), column VI is the same as column V, and if monovalent cations (e.g., K, Na, H) are present, column VI is twice that of V.

The number of cations in column VI corresponds to the cations per formula unit (per fixed number of oxygen atoms). A check on the balance of + and – charges in the formula provides a check on the arithmetic. From column VI, the formula can be written by assigning cations to the "ideal" formula. For example, because Al^{3+} can substitute for Si^{4+} in the tetrahedral sites, Al atoms (if present) are commonly added to Si in order to achieve ideal tetrahedral site occupancy. The remaining Al atoms are placed in the octahedral sites.

The steps above are summarized in the following table:

	I	II	III	IV	V		VI
	Weight percent oxides	mol wt	Molecular proportion of oxides	atomic proportion of oxygen from each molecule	number of anions based on 4 O [col IVx1.4792]		number of ions in formula
SiO_2	40.30	60.08	0.6708	1.3415	1.984	Si	0.992
Al_2O_3	0	101.96	0.0000	0.0000	0.000	Al	0.000
Cr_2O_3	0.02	151.99	0.0001	0.0004	0.001	Cr	0.000
FeO	8.85	71.85	0.1232	0.1232	0.182	Fe^{2+}	0.182
MnO	0.13	70.94	0.0018	0.0018	0.003	Mn	0.003
MgO	49.58	40.3	1.2303	1.2303	1.820	Mg	1.820
CaO	0.07	56.08	0.0012	0.0012	0.002	Ca	0.002
Na_2O	0	61.98	0.0000	0.0000	0.000	Na	0.000
NiO	0.42	74.7	0.0056	0.0056	0.008	Ni	0.008
Total	99.37			2.7041	4		3.008
		4/2.7041:	1.4792				

Formula: $(Ca_{0.002}Mg_{1.82},Fe_{0.182},Ni_{0.008}Mn_{0.003})_{2.015}Si_{0.992}O_4$

<u>Some general rules for writing mineral formulas.</u>

- Mineral formulas are written to provide structural information
- Cations are written first, followed by anion(s) or anionic groups
- Charges must balance (total cation charge = total anion charge)
- Cations in the same structural site are grouped together
- Cations in different structural sites are listed in order of decreasing coordination number (CN) (*Keep in mind that the ordering rules aren't always followed.*)

Example: $CaMgSi_2O_6$

Charge balance is maintained:

$$Ca^{2+} + Mg^{2+} + 2(Si^{4+}) = 6(O^{2-})$$
$$2 + 2 + 8 = -(12)$$

Cation size (and radius ratio) dictates CN of cations:

Si – 4-fold
Mg – 6-fold
Ca – 8-fold
$^{VIII}Ca^{VI}Mg^{IV}Si_2O_6$, where roman numerals indicate coordination of cations

If cations interchange with each other in a given site, then group these cations with parentheses:

$^{VIII}Ca^{VI}(Mg,Fe)^{IV}Si_2O_6$

or

$Ca(Mg,Fe)Si_2O_6$

Your mineralogy text should include a list or table of common ions and their typical coordination numbers. Also, use the general formulas as a guide for ordering the cations in the formulas. Figure 2 is a chart of cation occupancy for pyroxenes.

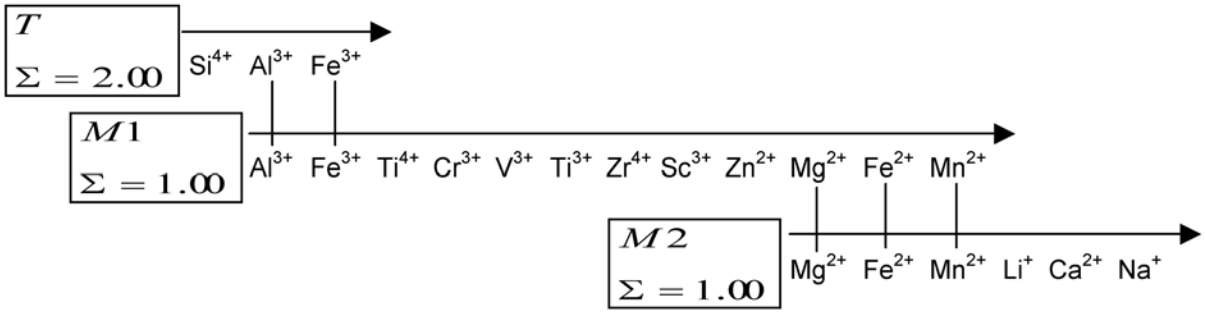


Figure 2. Flow chart showing ideal site occupancy and order of assigning atoms to T, M1, and M2 sites of pyroxene structure (modified from Deer et al., 1992 after Morimoto, 1988).

EXERCISE

<u>Problem #1</u>

In this exercise you will be working with electron microprobe data collected from a high-pressure mantle melting experiment. Figure 1 is a back-scattered electron (BSE) image of a run product from just such an experiment. In the highly magnified image you can see several different types of grains in terms of grayscale or "whiteness." The brightness (whiteness) in a BSE image correlates to the mean atomic number of the material under electron bombardment, thus the phases in the experimental charge can be differentiated based on their grayscale -- darker gray = lower mean atomic number, brighter (whiter) = higher mean atomic number. Practically speaking, the analyst positions the sample under the electron beam using the BSE image as a "map" and then analyzes the mineral (or piece of glass) of interest. This generally requires many hours sitting in a dark room. The good news is that I have done this for you!

The following microprobe analyses are from a high-pressure peridotite melting experiment (Schwab & Johnston, 2001) like the one shown in Fig. 1. These four minerals (olivine, orthopyroxene (opx), clinopyroxene (cpx), and spinel) are in equilibrium with glass (representing partial melt) at the pressure (1.0 GPa) and temperature of the experiment.

	Olivine	Ortho-pyroxene	Clino-pyroxene	Cr-spinel
SiO_2[1]	41.05	55.68	53.23	mdl
Al_2O_3	0.04	3.66	4.49	30.48
FeO*	7.92	5.10	3.74	9.08
MnO	0.14	0.11	0.12	mdl
MgO	48.70	32.54	22.18	18.32
CaO	0.34	2.71	14.61	mdl
Na_2O	mdl[2]	0.06	0.21	mdl
Cr_2O_3	0.26	1.27	1.72	38.49
Total	98.45	101.13	100.30	96.37

[1] Weight percent oxides, unnormalized
[2] mdl represents "below minimum detection limit"
FeO* = all iron as Fe^{2+}

Calculate and write out the formula for each of these four analyses. Base your calculations on the following definitions of mineral species:

Olivine: $(Mg,Fe)_2SiO_4$ → 4 oxygens per formula unit
Opx: $(Mg,Fe)_2Si_2O_6$ → 6 oxygens per formula unit [3 if using $(Mg,Fe)SiO_3$]
Cpx: $Ca(Mg,Fe)Si_2O_6$ → 6 oxygens per formula unit
Cr-Spinel: $(Mg,Fe)(Cr,Al)_2O_4$ → 4 oxygens per formula unit

Setting up a spreadsheet for these calculations is very useful!

<u>Problem #2</u>

X-ray diffraction studies of the cubic Cr-spinel (above) yield the following information regarding the crystallographic axes and unit cell dimensions for this mineral:

$$\mathbf{d_{(100)} = a = 8.23Å}$$

In addition, the density of this mineral has been measured to be 4.12 gm/cm^3. ***Calculate the unit cell content for this mineral***. The unit-cell-content is defined as the number of formula units contained in the unit cell of the mineral. **Hint**: Once the formula is calculated (Problem #1), calculate the volume of the unit cell (*cubic unit cell → a = b = c, all intersecting at 90°*) and the molecular weight (gm/mole) of the formula unit. With this information, you can then calculate how many formula units are present in the crystallographic unit cell by considering the following equation:

$$\textbf{Number of formula units} = V\rho N_A/\textbf{formula weight}$$

where V is the cell volume in cm^3, ρ is the density in gm/cm^3, N_A is Avogadro's Number (6.02 x 10^{23} mol^{-1}). Owing to uncertainties in the analysis, cell parameters, density, etc., the final number of atoms per formula unit and the number of formula units per unit cell should be rounded to the nearest whole number. **Helpful conversion: 1 Å = 10^{-8} cm, so that 1 cubic Å = 10^{-24} cm^3.

Problem #3

Mineralogists and petrologist often talk in terms of percent end member composition for minerals with solid solution. For example, "An_{55}" would refer to a plagioclase feldspar called "labradorite" with 55% anorthite ($CaAl_2Si_2O_8$) and 45% albite ($NaAlSi_3O_8$).

The Olivine Group is a solid solution series between magnesian *forsterite* (Mg_2SiO_4) and ferroan *fayalite* (Fe_2SiO_4). Use the Mg and Fe cation values you calculated in #1 to ***determine the forsterite content (Fo%) of the olivine***.

Problem #4

After determining the formulas of the two pyroxene analyses above, plot them on the following quadrilateral. You could take your calculated mineral formulas, write a reaction for each pyroxene using the three components ($Ca_2Si_2O_6$, $Mg_2Si_2O_6$, $Fe_2Si_2O_6$), normalize to 100%, and then plot the results. However, the difference between the three components is the cations: Ca, Mg, and Fe. You have already calculated the cation abundances above, so you can simply normalize the three cations to 100% and plot the percentages! ***Plot the two points on the quadrilateral***. Compare your plot to Figure 3. ***Provide a mineral name for each pyroxene. Are there any other significant chemical components in your pyroxenes? If so, what are they? Would the consideration of other components affect the naming of the minerals?***

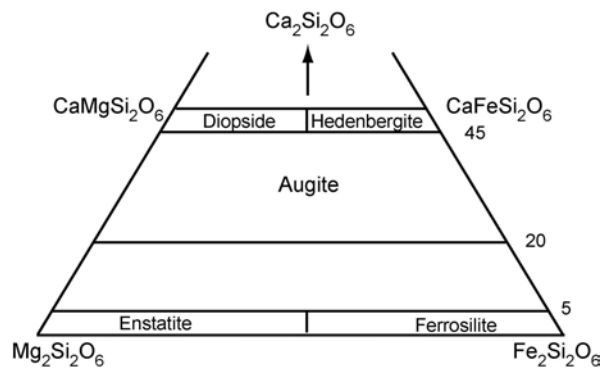
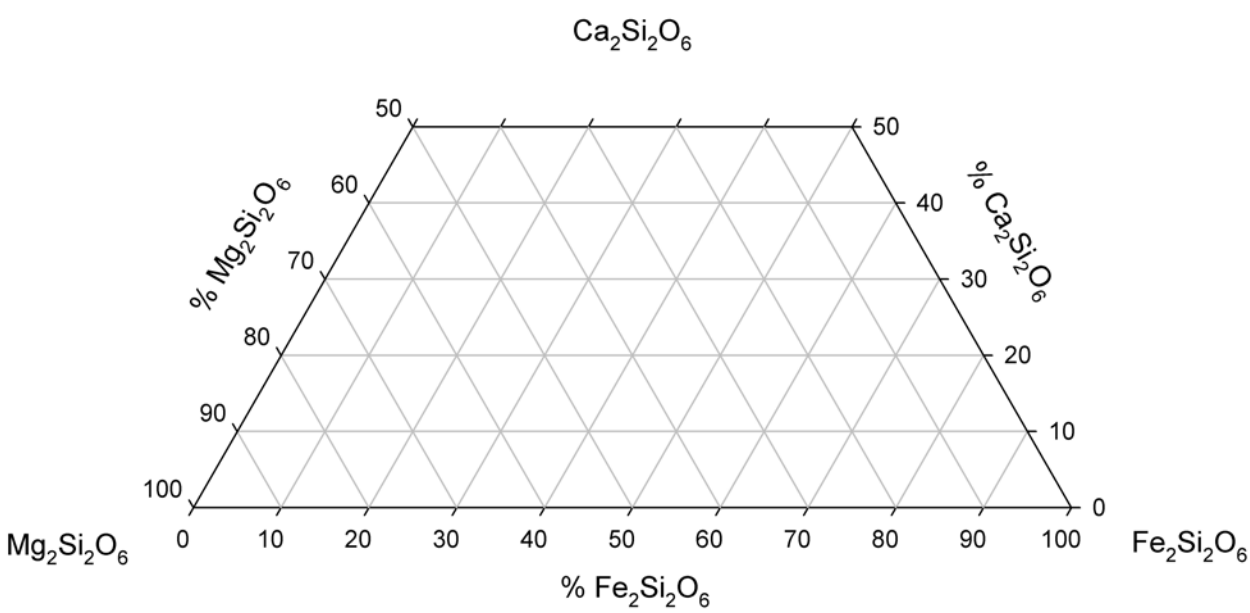


Figure 3. Classification of pyroxenes (modified after Morimoto, 1988 and Deer *et al*., 1992).



Problem #5

The mineral data that you used above came from a series of high-pressure (1.0 GPa) experiments investigating the melting systematics of peridotite. The coexisting pyroxenes (Opx and Cpx) in these experiments define a miscibility gap in temperature-composition space from 1235°C to 1360°C (Schwab & Johnston, 2000). As a result, the CaO content of the clinopyroxene in this sample can be used as a geothermometer. Using the following equation, calculate the temperature of last equilibration of the peridotite.

$$\text{Temp (°C)} = -2.0914x^2 + 44.164x + 1131.4, \text{ where } x = \text{wt. \% CaO in cpx}$$

What is the temperature of the experiment?

Give an example and provide a literature or web reference of another "geothermometer." What are the requirements and assumptions that must be made when using this geothermometer?

ACKNOWLEDGEMENTS

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