12.119 Problem Set 2: Electron Microprobe

Question 1: Characteristic x-rays

For the following elements decide which one of the three diffracting crystals would be best to use to measure the x-ray intensity. Recall that the optimal range of 2θ for each crystal is from 30 to 130 degrees and that the best peak shape is achieved closest to the middle of the 2θ range of the spectrometer. You'll also need to recall Bragg's Law $n\lambda = 2d\sin\theta$. We are typically most interested in the first order peaks (i.e., n = 1).

Diffracting crystals	**2d (nm)**
TAP	2.5757
PET	0.8742
LiF	0.4027

Element	**X-ray emission line**
Mg	K_α = 0.989 nm
Ca	K_α = 0.33584
Fe	K_α = 0.193735

Question 2: Quantitative analysis methods. Empirical Bence-Albee correction procedure.

MIT researchers Ziebold and Ogilvie (1964) found that in a binary system 1-2, the concentration (C) and k-ratio (the ratio of intensity on the sample to the intensity on the standard) of component 1 are related by the following equation:

$$(1-k_1)/k_1 = \alpha_{12}(1-C_1)/C_1 \quad (1)$$

or,
$$C_1/k_1 = \alpha_{12} + (1-\alpha_{12})C_1 \quad (2)$$

where α_{12} is the α-factor, a constant for component 1 in the binary system 1-2, at a given value of electron beam energy E_0 and take-off angle ψ. Bence and Albee (1968) applied the above to a system of n components. For the nth component:

$$C_n/k_n = \beta_n \quad (3)$$

where,
$$\beta_n = (k_1\alpha_{n1} + k_2\alpha_{n2} + k_3\alpha_{n3} + ... + k_n\alpha_{nn})/(k_1 + k_2 + k_3 + ... + k_n) \quad (4)$$

The value of α_{nn}, which is the α-factor of element n in itself, is unity.

In the following problem, the intensities of Mg, Si and Fe in standards and an olivine sample are given. Although we measure the intensities of the elements, the Bence-

Albee correction procedure calculates concentrations as oxides. The different alpha factors at 15 keV and 40^o take-off angle are also given.

Correction factor (CF) is the concentration of the oxides after correction for matrix effects. For our example, the standard intensities were taken using synthetic forsterite for Mg and Si and Marjalotti olivine for Fe.

Calculate the concentrations of MgO, SiO_2, and FeO in the sample by the following iterative procedure and using the data from the table below.

1) Using equation (4), calculate β for each oxide.
2) Using the β values from step 1, calculate a first approximation of C'_{MgO}, C'_{SiO2} and C'_{FeO} from the equation:

$$C_n = k_n \beta_n CF_n \qquad (5)$$

3) Calculate a new set of β values (β'_{MgO}, β'_{SiO2}, β'_{FeO}), using the first approximation concentrations (C'_{MgO}, C'_{SiO2}, C'_{FeO}) and the following equation:

$$\beta'_n = (C'_1\alpha_{n1} + C'_2\alpha_{n2} + C'_3\alpha_{n3} + ... + C'_n\alpha_{nn})/(C'_1 + C'_2 + C'_3 + ... + C'_n) \qquad (6)$$

4) Calculate new concentrations (C''_{MgO}, C''_{SiO2}, C''_{FeO}) using equation (5) and the new β values (β'_{MgO}, β'_{SiO2}, β'_{FeO}).
5) Repeat steps 3 and 4 until the differences between successive calculated β values are arbitrarily small. This happens after 3 or 4 iterations. Please show your work for each iteration.
6) The final calculated concentrations (in weight fraction) are determined using equation (5) and the final calculated β value.

	MgO	**SiO2**	**FeO**	**Total**	**comment**
I (std)	393.46	328.81	22.1		standard intensity
CF	0.5473	0.3364	0.1018		standard correction factor
I (sam)	323.72	320.26	14.41		measured intensity on sample
α_{n-1}	1.085	1.3	1.119		alpha factors: **Mg-Si, Si-Fe, Fe-Mg**
α_{n-2}	2.101	1.414	1.126		alpha factors: **Mg-Fe, Si-Mg, Fe-Si**