WHAT'S IN A MINERAL?

Extending Mineralogy by Electron Microprobe Analysis

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INSTRUCTOR NOTES:

This lab is designed to be a highly interactive lab session, where instructors provide a minimal level of essential background and then the entire group works together to explore mineral chemistry. In using a new piece of technology, students can "learn as they go". The point is not to understand every aspect of how an instrument works or to become proficient users, but rather to use the visual impact of the output to catch their interest and advance their analytical skills in the process. I find this lab works very well as a bridge between two semesters of a typical Mineralogy-Petrology sequence. Having completed crystallography, systematic mineralogy and optical, students find this a welcome change of pace and it helps them to start thinking about how mineral associations form the basis of petrology. It is also a great reinforcement and integration of mineralogy and chemistry, allowing you to leap off into crystal chemistry more deeply.

The main goals of this lab are to:

- introduce students to new technology and instrumentation
- introduce/reinforce concepts of x-rays and x-ray analysis techniques
- introduce concepts of image analysis
- reinforce learned mineral formulas and compositions
- understand how idealized formulas relate to the messy reality of solid solution and stoichiometry
- calculate a mineral formula from an oxide analysis, following simple rules of stoichiometry

Alternative formats for different lab set-ups:

- with a full EPMA
- with an SEM-EDS only
- with no instrumentation

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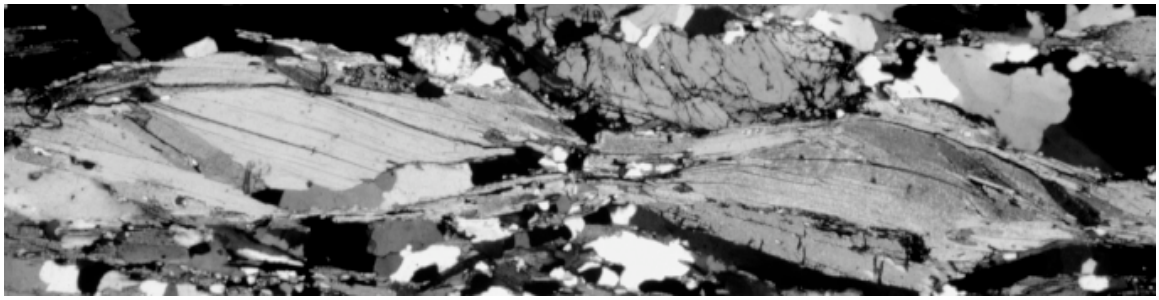

Thin section photomicrograph, muscovite-kyanite schist, Antarctica

Purpose: In this lab we will reinforce what you know about minerals by analyzing the chemical composition of some common minerals. We will use an instrument called an **electron microprobe**, which uses a tiny beam of electrons that interact with a solid sample. The interaction of the beam electrons and electrons in atoms of the mineral generates x-rays. X-rays of a particular energy and wavelength are characteristic for different elements; hence, if we can measure the x-rays we can determine the elements present. First we will use the microprobe to generate images (composition maps) of the minerals in a rock. Then we will identify as many minerals as we can simply from the proportions of chemical elements they contain. Finally, once we have identified some mineral unknowns using qualitative techniques, you will analyze them quantitatively, determine their actual formulas, and compare your analyzed compositions to the general formulas you learned before. Later, we will use your mineral analyses to determine the physical conditions during formation of this rock.

At the beginning of the lab period, proceed directly to the electron microprobe lab; do not pass "Go" and do not collect $200! In the probe lab, you will learn about the basics of the instrument (EPMA, for electron probe microanalyzer, or "probe" for short). We will then work with a rock sample to try to determine how many different minerals there are, try to get a qualitative idea of their compositions, and then measure a quantitative analysis of one or two minerals.

1. Qualitative EDS analysis

We will be working with a sample of a metamorphic rock from Antarctica (89GGR-33A). The microprobe generates a very fine electron beam that impinges on a "probe section". Probe sections are just like thin sections, only with a finer polish and no cover slip (we don't want to analyze glass!). The electron beam impinges on the surface of the mineral sample, and the transfer of energy from the beam to the atoms in the sample generates a set of "characteristic" x-rays for all of the elements in that mineral. Using an **energy-dispersive** detector system (EDS), we can look at a spectrum of x-ray energy levels and determine what elements are contained in the mineral of interest. We will do this in order to determine (a) how many minerals we have, and (2) the basic elemental composition of the mineral unknowns.

Where do we put the beam? To decide that, it's useful to have a map. We can sweep the electron beam across a small area of the polished sample (called "rastering"), which produces a variety of interactions that we can use to make maps of the sample surface. These include:

- *secondary electrons* (SE), which show surface texture,
- *back-scattered electrons* (BSE), which reflect the average atomic number of a substance,
- *cathodoluminescence* (CL), which yields visible-light photons,
- energy-dispersive *digital x-ray maps*, which generate images of element distribution.

Images produced by these interactions can be seen in real time or saved digitally for later use. We will use several of these techniques to map out the variety of minerals in our rock.

As you determine how many minerals occur in this rock using some of the imaging techniques described above, list the minerals that you think occur in this rock based on your EDS analysis. Consider not only the elements found but also their relative proportions (that is, Al vs. Si, K vs. Ca, etc.). You may wish to list some by specific names, and others by "Unknown" followed by a list of elements it contains.

Mineral	Elements	Mineral Name (if known)
a.	_____	_____
b.	_____	_____
c.	_____	_____
d.	_____	_____
e.	_____	_____
f.	_____	_____
g.	_____	_____
h.	_____	_____

As you see, collecting an EDS spectrum is quick and easy! However, the EDS only tells us what elements are present in their general proportions, and we don't get a measure of its true composition. For this we need to conduct quantitative analysis.

2. Quantitative analysis

Now that we have some idea how many minerals there are and what elements they contain, we can actually determine their chemical compositions. We use the **wavelength-dispersive** (WDS) capabilities of the microprobe to measure nearly any element in a solid material, which makes lab benches, titration columns and solvents nearly obsolete! The electron microprobe allows one to analyze the chemical composition of solid materials such as minerals and glasses in small volumes, typically much less than the size of an individual crystal. With a focused electron beam on a flat sample surface, one can routinely analyze areas 1-5 μm in size (1 μm = 1 micron = 10^{-3} mm = 10^{-6} m). This offers a level of spatial resolution that is very useful in studying changing mineral compositions as a function of P, T, fluid composition, oxidation, etc. For example, you can quantitatively measure compositional variation in a zoned crystal (think of oscillatory-zoned plagioclase, for example). The probe thus allows you to do mineral chemistry in the context of observable growth textures.

The basics of this analysis are just the same as for the EDS method, only in this mode the x-rays generated from electron bombardment are diffracted by a set of crystal spectrometers. The positions of the diffracted x-rays correspond to individual elements, and the numbers of x-rays in each position are counted to determine how much of that element there is. Normally this is done in reference to standards of known composition. You will be guided through the routine procedure for collecting a quantitative probe analysis.

During the analysis, you will obtain data measured in weight percent of the oxide of an element. This is an artifact from the days of wet-chemical analysis, when oxides were titrated, but it means that in order to derive a meaningful chemical formula for the mineral, you will need to convert these oxide compositions to elemental (or cation) proportions. This procedure is outlined in Klein & Hurlbut (p. 240-244).

3. Mineral formula recalculation

For two of the minerals that we analyzed by WDS methods, calculate their elemental abundances and determine chemical formulas. We will recalculate element compositions for two minerals using an Excel spreadsheet. As outlined by Klein & Hurlbut (p. 242), you need to determine:

a. molecular proportions
b. atomic proportions
c. cation proportions (assuming a given number of oxygen atoms per formula unit)

Note that we will assume a fixed number of oxygen atoms, depending on the type of mineral (for example, pyroxene can be assigned 6 oxygens, biotites have either 11 or 22, etc.). Also, we cannot use the microprobe to analyze for the different valence states of iron (Fe^{2+} and Fe^{3+}). So, we will make some simplifying assumptions about which and how much of these two species we have in each mineral. Attach a print-out of your spreadsheets with this lab.

Now, write an appropriate mineral formula for each mineral using the fractional proportions you determined above. When you do this, be sure to renormalize the metal cations to an appropriate total number of cations (for example, feldspars contain 5 metal atoms relative to 8 oxygens, so your cation proportions should total to 5!). Because we do not analyze for oxygen, assume a full complement of oxygen atoms in your formula based on a general one.

Mineral	Formula
_____	_____
_____	_____

Compare the formulas you determined with the standard formulas for minerals that you learned before. How do the actual compositions differ from the general formulas? What does this imply about the chemical nature of these minerals? What does it say about this method of analysis?

LAB RUN-DOWN

1. Title: What's in a mineral? Extending mineralogy by electron probe analysis.

2. Equipment needed:

   EPMA system (with SE, BSE, EDS and/or CL detectors), *OR*

   SEM system (with SE, BSE, EDS and/or CL detectors)

   Polished thin section(s) of rock samples (no cover slip!), either standard section or 1" rounds

   Vacuum-evaporative C coater

   Conductive C paint

   Image maps (transmitted-light scans of full thin section work well)

   Instructional diagrams related to electron-beam principles, energy-level shells, excitation principles, electron responses, etc.

   Excel worksheets for mineral recalculations

   Deer, Howie & Zussman *Introduction to the Rock-forming Minerals*

   Computer(s) running Microsoft Office (with Excel)

   Calculator (handy)

3. Special considerations (based on feedback from the Petrology Workshop, June 2003:

   a) I run this lab in two 2-hr lab periods, depending on enrollments and how many people can comfortably fit in the lab and see the displays. It works well to do it in two parts:
      - Part 1 in the probe lab
      - Part 2 in a computer lab working with data

   b) This lab can be run either with a full EPMA or SEM-EDS or neither, as follows:
      - With EPMA, can do imaging by SE, BSE and/or CL, followed by EDS spectral analysis and x-ray composition mapping, and finally quantitative WDS mineral analysis.
      - With SEM-EDS, can do imaging by SE, BSE and/or CL, followed by EDS semi-quantitative analysis; instructor to provide WDS analyses of key minerals for students to use.
      - With no instrument, instructor can provide hard-copy output of the imagery (see accompanying image files), EDS and WDS analyses, and have the students work with the data.

   c) I recommend a reading assignment ahead of time on instrumentation methods and/or mineral formula recalculation (both covered in Klein).

   d) How much do students need to know about the sample ahead of time? I assume they know nothing except that it is a polished sample of a metamorphic rock. Later, students do a lab

using the probe data they collect, but at this point it is not important they know the context, which takes away instrument time. One could easily place this sample in the context of a suite the students will study, with clear benefit, but it is not essential to the success of a stand-alone lab.

e) I choose samples based on the mineral assemblages we will look at later in a lab where students determine P-T conditions of metamorphism. In the samples I use, the students have been exposed to the major minerals and are familiar with their general compositions, but it is not necessary they have seen them before in hand specimen or thin section. Any igneous or metamorphic rock will do, but I recommend staying away from anything too fine-grained or with complex textural relationships (overgrowths, retrogression, disequilibrium textures, etc.).

f) It helps if students are already exposed in a prior Mineralogy course to calculating mineral formulae from chemical analyses. I recommend they do this with a simple mineral such as olivine or a sulfide, as outlined in a textbook such as Klein. As a Petrology instructor, you may want to plea with the Mineralogy instructor (if not you!) to cover this.

g) A useful device to complement the imaging possible on the microprobe is a PetroScope, essentially a modified microfiche reader equipped with various lenses and polarizing films to project on a screen or on the wall how rocks and mineral appear in thin section (both plane- and cross-polarized light). I find this to be a very useful device for group learning, because you can look together at the very thin section being studied. With a standard magnification you can see most of a thin section, which allows you to examine textural relationships, and at optional higher magnification you can focus on individual minerals. An optional retardation filter allows you to view the rock as if with a waveplate inserted, very useful for evaluating lattice preferred orientations and kinematic indicators. The PetroScope is available commercially and depending on options can run a few thousand dollars. I endorse their product with qualification – I have purchased two units (one at SMU and one at UMD) and both of them were delivered with damage or with incorrect assemblies, so buyer beware! Don't sign off until you're satisfied.

h) Attached are quantitative microprobe analytical data for two unknown minerals (minerals 1 and 5 in sample 89GGR-33A); the minerals are shown in the BSE image in Fig. 8 and the corresponding EDS spectra are shown in Fig. 9. These are WDS analyses presented in weight percent oxide format. Students can recalculate the analyses as mineral formulas using procedures outlined below, which is most easily done in a spreadsheet like those attached here. The original Excel spreadsheets, with separate sheets for students and instructors, can be obtained by sending an email request to jgoodge@d.umn.edu.

Abbreviations used:

EPMA	electron probe micro-analyzer
SEM	scanning electron microscope
SE	secondary electron
BSE	back-scattered electron
CL	cathodoluminescence
EDS	energy-dispersive spectrometer system
WDS	wavelength-dispersive spectrometer system

References:

Goldstein, J. I., et al., 1992, *Scanning Electron Microscopy and X-ray Microanalysis: A text for biologists, materials scientists, and geologists*: New York, Plenum Press (2nd Ed.), 820 pp.

Klein, C., and Hurlbut, C. S., Jr., *Manual of Mineralogy*: New York, Wiley & Sons (21st Ed.), 681 pp.

NOTES ON MINERAL RECALCULATIONS

Students can follow the guidelines outlined by Hurlbut and Klein (or other sources) to determine a mineral formula by hand, but it's a lot easier if done on a spreadsheet. Provided with the lab are Excel worksheets for determining formulae for garnet and biotite based on a standard microprobe analysis given as metal oxides. These are basic formulations that satisfy stoichiometry but do not account for valence state of iron or site assignments.

It is feasible to do the "hand's on" probe session in a 2-hour lab period. Students can do the mineral calculations during another lab session if scheduled, or this part can be assigned as homework. I recommend it as a follow-on lab the same week because instructors and students can work on this together as a group, and it gives students exposure to working with data in a spreadsheet environment.

In the spreadsheets provided, students need to input the results of their analyses by hand (wt% of the various oxides). Most probe output already presents the mineral analysis is terms of cation proportions, but this can be deleted for the students. Then it is a matter of determining molecular and elemental proportions for each element based on an assumed number of oxygens. The example worksheets show how Si is treated, and the remainder of the worksheet is left for the students to complete. Giving students a framework keeps them from going astray with formatting the spreadsheet, but they still need to understand and/or determine:

- molecular weights of oxides
- molecular proportions of the oxides
- element proportions of oxygen and metals

Finally, students can write a simple mineral formula based on their normalized compositions, for example in garnet:

$$(Fe_{2.47}Mg_{0.40}Mn_{0.03}Ca_{0.11})Al_{1.97}(Si_{2.94})O_{12}$$

A little further explanation can connect the mineral composition to simple site assignments, such as for tetrahedral, octahedral and interlayer alkali sites in biotite:

Normalized to 11 oxygens:

Site	Cations	# cations
Tetrahedral (T_{iv})	Si, Al_{iv}	3.00
Tetrahedral (Al_{iv})	Al_{iv}	1.00
Octahedral metal (M_{vi})	Fe^{3+}, Al, Cr, Ti, Mg, Fe^{2+}, Mn	2.83
Interlayer (A)	K, Na, Ca	0.97
Hydroxyl	OH, F, Cl	n.a.

Normalized to 7 cations:

Site	Cations	# cations
Tetrahedral (T_{iv})	Si, Al_{iv}	3.00
Tetrahedral (Al_{iv})	Al_{iv}	1.00
Octahedral metal (M_{vi})	Fe^{3+}, Al, Cr, Ti, Mg, Fe^{2+}, Mn	3.00
Interlayer (A)	K, Na, Ca	0.97
Hydroxyl	OH, F, Cl	n.a.

ELECTRON PROBE ANALYSES

Mineral #1

SiO2	36.54
TiO2	0.03
Al2O3	20.76
MgO	3.39
CaO	1.22
MnO	0.41
∑Fe as FeO	37.69
Na2O	0.03
K2O	0.01

Mineral #5

SiO2	33.13
TiO2	3.48
Al2O3	17.73
MgO	5.95
CaO	0.02
MnO	0.01
∑Fe as FeO	23.93
Na2O	0.13
K2O	9.09

Oxide	Element	Microprobe data	Molecular weight	Molecular proportion	Element proportion for O	Element proportion metals	Cations normalized to 12 oxygens	Normalized to 8 cations	Sites	Cations (12-O basis)
SiO2	Si	36.54	60.09	0.60809	1.21618	0.60809	2.961	2.943	T	2.961
TiO2	Ti	0.03	79.88	0.00038	0.00075	0.00038	0.002	0.002		
Al2O3	Al	20.76	101.96	0.20361	0.61083	0.40722	1.983	1.971	B	1.985
MgO	Mg	3.39	40.31	0.08410	0.08410	0.08410	0.409	0.407		
CaO	Ca	1.22	56.08	0.02175	0.02175	0.02175	0.106	0.105		
MnO	Mn	0.41	70.94	0.00578	0.00578	0.00578	0.028	0.028		
∑Fe as FeO	Fe	37.69	71.85	0.52457	0.52457	0.52457	2.554	2.539	A	3.098
Na2O	Na	0.03	61.98	0.00048	0.00048	0.00097	0.005	0.005		
K2O	K	0.01	94.20	0.00011	0.00011	0.00021	0.001	0.001		
	Total	**100.08**			**2.46454**	**1.65306**	**8.049**	**8.000**		
				Norm factors:	4.86906		0.99393			
									A = Fe2+, Mg, Ca, Mn	
NOTES:									B = Al, Ti	
									T = Si	

Oxide	Element	Microprobe data	Molecular weight	Molecular proportion	Element proportion for O	Element proportion metals	Cations normalized to 11 oxygens	Normalized to 7 cations	Sites	Cations (11-O basis)
SiO2	Si	33.13	60.09	0.55134	1.10268	0.55134	2.647	2.711		
TiO2	Ti	3.48	79.88	0.04357	0.08713	0.04357	0.209	0.214	T(iv)	3.00
Al2O3	Al	17.73	101.96	0.17389	0.52168	0.34778	1.670	1.710	Al(iv)	1.00
MgO	Mg	5.95	40.31	0.14761	0.14761	0.14761	0.709	0.726		
CaO	Ca	0.02	56.08	0.00036	0.00036	0.00036	0.002	0.002		
MnO	Mn	0.01	70.94	0.00014	0.00014	0.00014	0.001	0.001		
∑Fe as FeO	Fe	23.93	71.85	0.33305	0.33305	0.33305	1.599	1.638	M(vi)	2.83
Na2O	Na	0.13	61.98	0.00210	0.00210	0.00419	0.020	0.021		
K2O	K	9.09	94.20	0.09650	0.09650	0.19299	0.927	0.949	A	0.97
	Total	**93.47**			**2.29124**	**1.62104**	**7.782**	**7.971**		
				Norm factors:	4.80090		1.02429			
NOTES:									T = Si, Aliv	
									M = Fe3+, Mg, Al, Fe2+, Cr, Ti, Mn	
									A = K, Na, Ca	