COMPREHENSIVE MICROPROBE ANALYTICAL STRATEGY (2014 update)
(written to assist Cameca SX 100 users at the University of Arizona)

OK, you've got your thin section, epoxy mount, or rock billet in the microprobe and one or more analytical routines set-up to analyze most, if not all, of the minerals present. You're sitting in the pilot's seat... now what?

Many times, beginning users of the microprobe lose track of the bigger picture and get caught up in all sorts of diversions. Sometimes it's hunting down every little bright white (high atomic number ["high z"]) inclusion you see (which can be very interesting, but it's not usually an efficient use of time)... sometimes it's analyzing a single grain a dozen times when the BSE image shows little to no zoning... sometimes it's missing an entire major mineral or two simply because your eye wasn't drawn to it (this happens especially when the brightness and contrast are not well-adjusted, and can be particularly problematic for darker, low atomic number ["low z"] minerals) that may "disappear" into a dark background.

These are all common pitfalls. Of course, depending on your specific goals, there might be reasons why you'd want to spend time looking for all the high z inclusions, or spend time analyzing the same mineral over and over, or blow off spending time on minerals that are outside of the scope of your study. But in general, when you're just starting on a new sample, you're going to want to have a representative survey of the diversity of compositions of all the phases present, and how those compositions relate to textures and timing.

So, let's begin:

BEFORE YOUR MICROPROBE SESSION:

1) Do your petrography. This first step is written primarily with transmitted light petrography of polished (not covered!) thin sections in mind. If you're looking at epoxy mounts or polished billets instead, you're limited to only reflected light petrography, which is optimal for opaque minerals but not so great for most silicates. Unless time or cost constraints are an issue, or your samples are primarily sulfides or oxides, it's best to have polished thin sections prepared for maximum flexibility.

Identify all of the obvious minerals, and take notes on ones that you're unsure about. Take notes on dominant textures, intergrowths (especially ones that might indicate timing relationships or might be useful for P, T, X calculations), veins, and alteration.

In some cases, you might have a BSE image or set of X-ray maps to provide additional mineralogical or chemical data.

One reason for good petrography in advance is that it can be very challenging for a beginning microprobe user to identify even common minerals from an EDS spectrum alone. For example, you might see Mg, Si and O peaks on the EDS spectrum, but is the mineral forsterite, enstatite, talc, serpentine, cummingtonite, or even something else? You might say, "It's not important... I can figure it out later". Maybe, but that can be a very unfortunate choice: let's say you get a 97% total on this mystery Mg-silicate... is that a good or bad total? Well, it could be a good amphibole analysis (remember the non-analyzed OH in amphibole), but it would be a terrible olivine analysis. And you don't want to spend the entire day collecting bad data! And even if the analysis turns out fine, also consider this: if you don't know what mineral you've analyzed, think about how long it would take to test *every* normalization routine you would have to try to ultimately calculate its correct formula.

As an important reminder, microprobe work can only be done on samples that are uncovered and well polished... the higher quality the polish, the better chance for high quality analytical data. Thin sections for microprobe analysis ideally should be polished down to a 0.25 to 0.3 μm diamond or alumina grit size.

2) Identify general regions of interest (ROI) in the thin section. These areas might include unique or unusual minerals, minerals that appear to be chemically zoned (either optically or from BSE or X-ray map data), features such as veins and vein envelopes or overgrowths that show timing or reaction information, minerals or mineral intergrowths of P, T, X value, or any minerals you weren't able to identify optically. Depending on the complexity of these areas, you'll usually want to limit yourself to ~3-5 ROI. Of course, selecting these areas does not preclude you from examining other thin section areas if microprobe time allows.

3) In the past, I used to recommend carefully drawing circles with an ultra-fine-tip Sharpie or Rapidograph pen around your ROI. However, this was not always an easy process, and sometimes the circle would miss the critical features you wanted to highlight, or worse, would accidentally cover them in ink. Today, with the ubiquitous availability of high megapixel cameras on cellphones, it's much easier to simply take a high-resolution photo of the thin section and print out the photo. This will act as your map. (By the way, to avoid wasting a lot of printer ink on the dark areas [and to make hand-written annotations easier to see], you can adjust the "transparency" in most photo-editing programs to fade the image to a pale, low-contrast set of grays [or colors] prior to printing).

4) If possible, photograph the ROI under both PPL and XPL. In some cases, you may also want to photograph the areas in reflected light. Key the images to your ROI areas. For example: "image_0001: area 1, biotite with apatite inclusion, PPL", "image_0002: same, in XPL", etc. You should maintain a consistent orientation of the thin section (the way you plan to put it into the microprobe) for all of your photographs.

5) Locate and mark the locations of your ROI photos on your whole thin section map.

6) If you plan to view the photographs on your computer at the microprobe (recommended, if possible), rotate them so they will match the images seen on the microprobe. If you opt to print them out instead, rotation is not necessary. Depending on how the camera is turned on the microscope, rotation may also not be necessary. Just keep in mind that the image you see through the oculars (not necessarily on the computer) will be rotated from what you'll see on the microprobe.

7) With a dry KimWipe, carefully wipe the thin section to remove fingerprints. You can use a little bit of pressure. Once you clean the thin section, be careful not to introduce any new fingerprints. You especially don't want to lock dirt and grime underneath the carbon coat.

AT THE MICROPROBE:

8) Carbon-coat the thin section (verify that you're carbon-coating the correct side). Coating can be done on the morning of analysis, or beforehand. Generally for the first pair of thin sections you plan to examine in the morning, it's useful to carbon-coat them the day before. You can take advantage of that advance visit to the microprobe to verify with Ken what time you plan to arrive and which analytical routines you'll need calibrated for the morning.

9) Once the thin section is in the holder (right side up, and oriented the same way you mapped it), use the thin section grid overlay to simplify finding the approximate coordinates of the various ROI. Mark these coordinates on your map; these will guide your navigation. If the thin section holder is not in use, this can also be done in advance.

10) One or more various "routine" analytical programs will generally be calibrated for you before you arrive (although you can certainly calibrate them yourself, or put together new programs to suit your particular needs). Ideally, you should analyze at least one standard first for each program you'll be using to verify that the calibration is acceptable. Pay attention not only to major elements but to minor elements as well. The general silicate routine can be tested on Kakanui hornblende. The apatite program can be tested on Maria (or Wilberforce) apatite. The epidote and titanite routines can both be tested on BLR-1 titanite. When in doubt, ask about what the currently available "test" standards are and what their major and minor element compositions are.

11) Locate your first ROI in BSE under low magnification. Ensure the reflected light optical view is in focus, and that the BSE image is sharp and crisp (you may need to significantly increase the magnification to check this). Ensure that the brightness and contrast are adequate to give you a good overview of the complete mineralogy of the area. In general, the lowest z minerals (typically quartz, albite, aluminum silicates, some clays, talc or serpentine) should be a dark shade of gray (but not quite black... otherwise, slightly increase the brightness and/or decrease the contrast), and the

highest z minerals (typically sulfides or Fe-oxides, or zircon) will be nearly white; most other common minerals will be intermediate shades of gray. Only epoxy should be black (and should be avoided during analyses). How many different shades of gray do you recognize? In some cases, other contrast and brightness setting will be useful, particularly to accentuate subtle shading differences between two different minerals of similar z. Use your photographs to assist you in identifying and differentiating minerals.

Sometimes it is useful to use the microprobe's optical microscope (either reflected light, transmitted PPL or XPL) to navigate or verify your location. However, I find that the BSE image, once you get used to the shades of gray, is a lot simpler (and is capable of a lower magnification as well... useful for seeing more of the thin section at one time). Keep in mind that the transmitted light images (especially the XPL images) on the microprobe are not as good as those from a petrographic microscope... indeed, nominally isotropic minerals or minerals in extinction appear purplish rather than black under the microprobe's version of XPL. Before you set up an analysis, remember to always check the reflected light view to ensure you're in optical focus... analyses done on out-of-focus samples yield bad totals.

12) If necessary, spend a few minutes to verify your optical microscopy by doing EDS spectra on the phases present. It is customary to start with the darkest (or brightest) shade of gray, and systematically checking each intermediate shade in order. Be sure to differentiate between zoning within one mineral, versus an intergrowth of two or more minerals... this distinction can sometimes be difficult to discern. Occasionally, the same or nearly the same shade of gray can represent two or more different minerals (e.g. titanite and apatite; magnetite and zircon), so test several examples (particularly grains of different sizes or morphologies) to verify how many phases you're really dealing with (incidentally, apatite and zircon are usually noticeably strongly cathodoluminescent even at relatively low magnification, so this property can be useful to quickly differentiate these minerals from titanite and magnetite, respectively). EDS spectra aren't normally saved, but if you run across a mineral you can't identify, it is worthwhile to either save the spectrum or at least print it out. Obviously, be sure to label it well and reference it to your map: labels such as "spectrum #3", pointing to a specific location on a BSE image or thin section photo can be invaluable. Alternatively, if all the EDS peaks of the unknown mineral correspond to elements that are part of your analytical routine, you could simply analyze it.

13) Identify specific areas you want to analyze. Minerals with nominally stoichiometric formulas and little to no expected compositional variability (such as quartz, corundum, kyanite, etc.) are not usually worth analyzing, unless you're specifically set up to look for minor or trace components. If compositional zoning is present (in some cases you may need to turn up the contrast, and turn down the brightness to see this), analyze each major compositional zone. Core and rim analyses (or multi-point core to rim traverses) are sometimes interesting in minerals that are known to exhibit that type of compositional variability. Don't spend too much time on multiple analyses if compositional variability isn't obvious in high-contrast BSE imaging... a couple of points is usually adequate. For minerals pairs used for P, T, X

calculations, analyze both phases roughly 10 μm from the boundary (to avoid accidental subsurface overlap). Note that at present, the true beam position is roughly 2 μm to the right of the "+" marker in BSE viewed with the "66 micron" setting, so be aware of that offset when trying to very precisely position the beam on a thin zone or near a grain boundary (this may change over time, so ask about the most recent offset if you're unsure or haven't visited the microprobe in several months). The number of spots you ultimately analyze will depend in part on the complexity of the sample, and time constraints. Nonetheless, more points tend to yield better analytical statistics. Keep in mind that some of the same minerals may occur among several of your ROI, so you may have an opportunity to collect numerous data points on the same mineral from disparate areas of the thin section. In some cases, a mineral grain may be so rare and so small that you'll only be able to analyze one spot on it (or even no spots if it's too small... less than ~10-15 μm... be aware that such small grains often yield poor totals and odd stoichiometries).

For the comments for each analysis, use descriptive text. List the thin section name (if you anticipate doing more than one thin section), the area number, and a detailed phrase describing what you're looking at. Spaces, commas, periods, hyphens, etc. are all allowed and are encouraged to make readable text. Useful comments include, for example: "highest z zone in garnet", "hbd from hbd-plag pair 1" or "secondary titanite rimming ilmenite, next to biotite". There is a limit to the total characters you can use in your comments, but it's fairly large, so be generous and informative with your descriptions, but start with the most important information first lest the end gets cut off.

As you are doing analyses, keep an eye on the totals and the various element concentrations. Here are some pointers:

Totals for anhydrous minerals with no Fe^{3+} or Mn^{3+} (assuming Fe and Mn are treated as "2+" cations) should be at least between 99 and 101 wt%, and ideally between 99.5 and 100.5 wt%. Totals that are anomalously low (below 98.5 wt%) may represent hydrous minerals, minerals with significant Fe^{3+} or Mn^{3+} (i.e. magnetite, epidote, andradite, piemontite), minerals with generally non-analyzed light elements such as Li, Be, B, N, C (note that H, He and Li are impossible to analyze for, and Be, B, N, C and O are challenging and are not routinely sought), minerals with other significant elements that were omitted, a poor focus (this is an insidious problem if you're not diligent about checking the focus before each analysis), a beam-sensitive mineral (look for specimen damage), or simply a poor calibration. Anomalously high totals (greater than 101.5 wt%) are more unusual, and indicate either a poor calibration, an interference (such as apparent V and/or Ba counts in Ti-bearing minerals... see discussion at step #19), or element migration in a beam sensitive mineral. This latter issue is commonly observed in analyses of F-rich apatite and Na-rich framework silicates (e.g. Na-rich plagioclase, sodalite, scapolite). If you expect a total should be near 100% and it isn't, take a minute or two to figure out what the problem is... there's no sense spending an entire day collecting bad data.

In addition to major elements and totals, pay attention to trends in minor elements too:

K-spar and micas almost always contain some Ba (but note that in Ti-rich minerals, some of this apparent Ba may not be real);
igneous micas and amphiboles almost always contain some F, Cl and Ti;
clinopyroxene almost always contains some Mn, Ti, and detectable Sc, V and Cr;
igneous forsterite almost always contains some Ni, and may contain detectable P;
igneous apatite almost always contains some LREE, and sometimes Mn, Sr and S;
igneous titanite almost always contains some Al, Fe, F, LREE, Zr, Y and Nb;
epidote almost always contains some Sr, and may have detectable V and Sc;
pyrite commonly contains detectable Co;
igneous ilmenite almost always contains minor to notable Mn;
staurolite and igneous tourmaline commonly contain detectable Zn;
igneous "pyralspite" garnet commonly contains detectable Na, Y, Sc, P and F; in contrast, grossular and andradrite may show little to no minor elements.
intermediate to calcic plagioclase commonly contains detectable Sr and P;

These are a few of many examples. Although there are certainly many exceptions to these general observations, suspect something may be wrong if you can't detect these elements in appropriate standards, or if you consistently never detect these minor elements (or other expected minor elements), even from among diverse thin sections. When in doubt, always verify with a standard known to contain that element.

Note that for beam sensitive minerals, the use of a slightly defocused beam (<10 μm, or alternatively, very slowly moving the sample during analysis... works best for unzoned minerals) can mitigate some sample damage and markedly improve totals.

Analyses of fluorapatite crystals where the c-axis is perpendicular to the plane of the thin section (hence, you can often see the hexagonal crystal outline) typically yield unrealistically high F values and totals >100%, whereas crystals aligned with the c-axis parallel to the thin section (enlongate prism sections) usually give better results. If possible, look for this latter orientation. Also with regard to apatite, the F Kα peak nearly overlaps with the 3rd order P Kα peak on the TAP crystal, and on occasion this complexity results in the location of the wrong F peak position during the critical calibration process, even in differential mode (note: this is a calibration error, not a user error). Be wary if F in apatite is routinely greater than 3.4-3.5 wt% (the theoretical upper limit), particularly in samples with more than 0.5 wt% Cl. If there is reason for concern, do a wavelength scan for F and verify the peak position you're using; if it's incorrect, a new calibration will be necessary. This may be an issue only in P-bearing minerals; normal silicates like amphibole and micas are not affected.

Analyses of pyrite, arsenopyrite and related MX_2 and MYX sulfides require calibrations of Fe and S in pyrite; analyses of chalcopyrite, pyrrhotite and other MX sulfides require calibrations of Fe and S in troilite. Analyzing pyrite (or arsenopyrite) using a troilite standard gives totals 1-2% high, while analyzing pyrrhotite (or chalcopyrite) using a pyrite standard gives totals ~2% low. Similarly, garnets should be analyzed with garnet

standards, if convenient; using other standards (especially for Al) sometimes yields totals that are 1-2% high. This is sometimes also observed in pyroxenes. The reason for these anomalies is not entirely clear but may involve slight peak shifts between the standard and the analyzed minerals; in general, standards should match the intended minerals to be analyzed as closely as possible for the best results, although perfectly-matched standards may not always be practical or time-effective. In any case, always keep an eye out for unexpected totals, and strive for the best possible results.

When the analysis is complete, re-set the current to 20 nA (if necessary), optimize magnification, brightness and contrast (if necessary), and move efficiently to the next location for analysis. Other than a quick glance at the previous analysis total to ascertain quality, you should not spend much time looking at the previous analysis *before* you've started the next spot. Each general silicate analysis (which includes a selection of minor elements) takes about 6 minutes, so there's plenty of time to look over the previous analysis (and also to plan out the next one) during the data collection period on the current one. If you're reasonably efficient, you can expect to spend ~50% of your time actively collecting quantitative data (the remainder of the time is spent moving, taking images, adjusting beam conditions, changing samples, etc.)

14) When you've completed your analyses in one area, optimize the image quality, slow down the scan rate, and take a picture of the area using the microprobe software. The software will also allow you to locate the analytical spots on the image. This image, with accompanying analytical spots, should be saved, as it is useful to later view the locations of your spots for data evaluation, and may be useful for publication too.

15) Move to the next ROI and repeat steps 11-14.

16) It is often worthwhile to slowly traverse the thin section at relatively low magnification in BSE to locate other areas of interest that you did not identify optically. I tend to do this either while I'm moving from one ROI to another, or at the end before I move to the next thin section. You may notice unusual BSE shading indicative of a previous unidentified mineral. A quick EDS spectrum of such finds will rapidly determine whether it would be worthwhile to further quantitatively analyze that phase. I tend to mark these additional analytical spots with a lettered area label, such as, for example, "area A, chromite core within magnetite" or "area B, very high z zone in epidote", to differentiate these last-minute ROI selections from those originally located. Images of these additional areas should also be captured (see step 14) and added to the thin section map.

One interesting technique that uses the low magnification scan is a search for high z phases in BSE. First, a fairly abundant, nearly white in BSE mineral is located. The brightness is then decreased (often the contrast is simultaneously increased, although this is primarily to accentuate subtle zoning) until the white mineral is a moderately dark shade of gray. At this point the thin section can be scanned for other phases that are now bright white. This process can be repeated with the new phase to identify even higher z phases. Note that in ore-bearing samples, galena, lead sulfosalts, bismuth

tellurides, and (rarely!) native gold or PGE are among the highest z minerals to be found. In sulfide-free rocks, monazite, barite, and occasionally tungstates (scheelite, wolframite) are among the highest z minerals commonly found.

17) In some cases, at the end of the day, it may be worthwhile to do a set of overnight WDS X-ray maps of your thin section, if these have not already been done. Keep in mind that these X-ray maps take several hours to run and thus can be expensive (remember, you're charged by the hour!) X-ray maps tend to be most useful if there are complex or fine textures, or fine-grained minerals (especially alteration minerals) that are not easily elucidated by optical microscopy.

AFTER YOUR MICROPROBE SESSION:

18) Typically the next day, your data will be available to pick up, either by visiting the microprobe lab with a flash drive, or by logging on and retrieving your data by FTP (you'll need a password to log on to the system). Don't forget to pick up your thin sections. The carbon coat is relatively robust but can be removed with a 0.3 μm polish. If you plan to spend more time on the microprobe in the near future with the same thin sections, it's easiest to just leave the carbon coat on. Repeatedly coating and then removing the coating can sometimes be rough on some samples, and removing all of the carbon from cracks and crevices can require some effort. Nominally, you want to do all your petrography and photography before you coat the sample the first time.

19) Mineral analytical data is customarily normalized (see the accompanying "setting up mineral normalizations in Excel" PDF for more details). It is easiest to copy just the comments, analysis numbers, and element (not oxide) wt% data (along with column headings) to a blank worksheet. The element wt% columns can be re-ordered to match the element order in your normalization spreadsheets (I personally prefer ordering by increasing atomic number). The individual sample rows can also be sorted, first by mineral type, and then by increasing analysis number. This easily facilitates copying blocks of data from this worksheet into your various normalization spreadsheets.

Note that some of the data will need minor adjustment in your spreadsheets. For example, the measured V Kα peak is slightly overlapped by the tail of the Ti Kβ peak, and the Ba Lα peak is similarly slightly overlapped by a Ti peak (particularly notable in rutile, ilmenite and titanite, due to their high Ti concentrations). These interferences are unavoidable, and result in *apparent* V and Ba concentrations that are larger than their true values. Although it is possible to set up the microprobe to automatically correct for these interferences (which has the advantage of simultaneously tweaking the PaP or ZAF corrections), it is usually acceptable (and much easier) to reduce the "excess" V or Ba yourself within your spreadsheets. In these examples, apparent V should be reduced by 5.4% of the Ti concentration to give true V, and apparent Ba should be reduced by 1.9% of the Ti concentration to give true Ba. Include appropriate IF statements in your formulas to avoid accidental negative values for the "true" concentrations (negative values should be forced to 0). Be aware that there may be

other examples of these types of interferences as well (e.g. apparent Na in nominally Na-free Zn minerals). I personally like to report the *uncorrected* V and Ba data along with the other element concentrations (although I italicize these uncorrected values and format them in gray to remind me they are uncorrected), and then apply the correction in the next set of cells as part of the first set of overall calculations (calculation of raw moles). However, you may find a different procedure works better for you, but be consistent.

20) Use your mineral normalization data to calculate P, T, X parameters of interest.

Consult articles in a current issue of American Mineralogist or The Canadian Mineralogist (the latter frequently has good examples for sulfides) for examples on how mineral compositional data are routinely presented in publications. In general, for oxygen-bearing minerals (oxides, silicates, phosphates, carbonates, etc.), oxide wt% data is followed by site occupancies of normalized atoms per formula unit; for sulfides and sulfosalts, element wt% data is followed by site occupancies of normalized atoms per formula unit.

Hopefully this guide will help you get the most out of your microprobe analytical experience. Happy and successful analyzing!