

**EPMA QUANTITATIVE COMPOSITIONAL MAPPING AND ANALYSIS OF LUNAR SAMPLES.**

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**Introduction:** We present the first fully quantitative compositional maps obtained by electron microprobe stage mapping on lunar samples, and summarize advances in measurement and quantitation procedures.

Electron-probe microanalysis (EPMA) is used for collection of point analyses, backscattered-electron (BSE) images, and x-ray intensity maps in the study of lunar, planetary and meteoritic samples. The silicon-drift energy-dispersive spectrometer (EDS), coupled with spectrum imaging software has enabled beam-raster mapping and phase analysis via data extraction tools. WDS stage mapping provides wide-area coverage on samples with superior peak to background, light-element, and trace-element detection compared to EDS. Commercial systems require time-consuming explicit background measurement by acquiring stage maps with the WDS tuned to background positions; for a 10 element setup this requires 30 maps to be acquired. Further, most software uses a linear conversion from x-ray intensity to concentration instead of a full  $\Phi(\rho z)$  correction. We discuss improvements using new software algorithms and detail use of Probe Software programs Probe for EPMA (PFE), Probe Image, CalcImage, and Golden Software program Surfer to perform the mapping correction.

**Analytical Procedures:** The same PFE WDS analytical setup used for point analyses is also used for stage mapping, so that a common set of calibration intensities is used for quantification of both point and map data. Typical conditions are as follows. Maps are acquired with 400-1024 pixel dimensions, with the electron beam diameter set to match the stage step size (0.X-15  $\mu\text{m}$ ), and probe currents of 50-100 nA with count times of 10-100 msec are used. Large areas can be covered by selection of appropriate pixel resolution and step size and can be coupled with a mosaic data collection mode. Higher probe currents partly compensate for reduced x-ray intensity at short dwell times, but quantitative mapping is precision limited, compared to conventional point analysis which is area limited.

We use a primary standardization where several potential standards are used for a given element and other standards with a range of average atomic number Z are used to generate a per-element set of empirical mean atomic number (MAN) background calibrations. The MAN calibration is iterated with composition in the ZAF correction loop and provides a remarkably robust estimator of background intensity for quantitative analysis. The use of MAN backgrounds in stage mapping provides an accurate background and eliminates the need to collect off-peak WDS backgrounds. The PFE

software performs a dead-time correction which is important for high-current mapping applications, and can include peak interference and other corrections as needed. Stage maps are acquired using the Probe Image software. On the Washington University JEOL JXA-8200 electron microprobe with 5 WDS, two passes are used to acquire data for 10 elements, and the x-ray intensity data are saved with 32 bit resolution.

**Quantitative Correction of Map Data:** The map intensity files are used as input to the CalcImage program to perform the full  $\Phi(\rho z)$  correction at each pixel, thus correcting for atomic number, x-ray absorption, and characteristic fluorescence effects. The backgrounds are subtracted using the MAN fits for each element, and the  $\Phi(\rho z)$  correction is performed relative to calibration standards from the corresponding microprobe run, thus providing traceability between map and point analytical data. The output is a set of map files for each element with concentrations units. For a 1024x1024 stage map, the mapping time is typically 10-20 hours and the conversion to corrected concentration maps requires about 2 hours depending on the clock rate of the computer. The CalcImage program is used to generate Basic language script files which are used by the Surfer program to plot the maps, contour the element levels in each concentration map, and to perform cross-section, polygon outline, and strip extraction of data from the maps. The polygon outline script allows a feature to be isolated and the remaining data blanked in the map. CalcImage is then used to perform cluster analysis of the map concentration data and can produce maps of the identified clusters. For the analysis of fine-grained extraterrestrial materials, a very useful and exciting capability is that cluster compositions can be coupled with user-specified phase density values to produce the density-corrected calculation of local bulk composition from a complex multiphase sample.

**Applications to lunar samples:** Lunar meteorite Miller Range 05035 was used to evaluate the capabilities of quantitative stage mapping (Fig. 1). MIL05035 is a low-Ti mare basalt containing complexly zoned pyroxene, maskelynite, and symplectite regions made up of silica, fayalite, and hedenbergite [1-2]. The coarse-grained phases and fine-grained symplectite intergrowth were used for large and small scale mapping, respectively. A large-scale Ca concentration map is shown in Fig. 2, with a conventional RGB x-ray intensity map for comparison. This map can be used to analyze the pyroxene chemistry, but can also be used to locate minor phases such as apatite which are difficult to find solely by BSE.

The symplectite region of MIL05035 (Fig. 1B) is thought to represent the breakdown of pyroxferroite [3]. A small-scale quantitative map was acquired at 512x512 pixels and 1.5  $\mu\text{m}$  pixel size, and processed to calculate the average composition. Table 1 compares estimates of the composition using (1) WDS defocused beam analysis (DBA), (2) EDS 300x raster averaging [4], (3) the quantitative map results from this study, (4) modal estimate from Fig. 1B BSE using ImageJ, and (5) modal estimate from BSE data of Liu et al. on a MIL05035 symplectite [2]. The limited area covered by DBA requires many replicates, while EDS raster analysis can analyze a larger number of grains. Both methods measure a heterogeneous sample, but use the  $\Phi(\rho z)$  correction which assumes homogeneity, so there are correction errors depending on the degree of chemical heterogeneity.

The quantitative mapping method performs a full analysis at each discrete point in the map and avoids the averaging problems associated with DBA and raster analysis. The column 3 data are therefore the best area estimate of the symplectite composition. All map measurements are by definition area measurements, but for calculation of the multiphase bulk composition it is necessary to correct for phase density. The modal estimates combined with average analyses of the phases from point EPMA measurements, have been used to calculate a modal recombination which includes a density correction (columns 4 and 5). The density-corrected compositions exhibit higher Fe but lower Si and Ca, reflecting the greater contribution from fayalite due to density. While the mode is based on a high resolution BSE image, the use of average phase compositions is a limitation to that approach.

Cluster analysis shows excellent promise for classification of phases and use as a measure of modal abundance. It is necessary to provide cluster definitions that discriminate phase identification so that cluster assignment is specific to a mineral. This allows the quantitative stage mapping to generate chemical and modal data for further analysis.

Table 1. MIL05035 symplectite area analysis

	1	2	3	4	5
SiO <sub>2</sub>	49.59	50.35	49.02	47.75	46.5
TiO <sub>2</sub>	0.43	0.52	0.47	0.35	0.39
Al <sub>2</sub> O <sub>3</sub>	0.58	1.18	0.64	0.30	0.27
MgO	1.86	2.00	2.19	1.77	2.13
CaO	6.39	6.65	5.88	5.12	5.79
MnO	0.59	0.59	0.78	0.66	0.63
FeO	40.47	38.2	40.88	44.02	44.0

1. WDS DBA: 50 spots, each 80 grains, 4000 total grains  
 2. EDS raster: 50 areas at 300x, 50k grains per area, 2.5x10<sup>6</sup> total grains  
 3. Quant. stage map 512x512 at 1.5  $\mu\text{m}$ , ~ 100k total grains  
 4. Modal estimate using BSE image Fig. 1B, with density correction  
 5. Modal estimate Liu et al., symplectite bk2

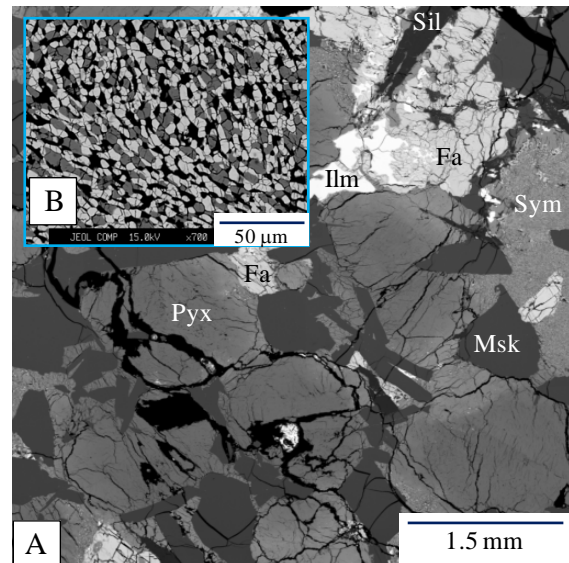


Figure 1A Backscattered-electron stage map of MIL05035. Complexly zoned pyroxene (Pyx), maskelynite (Msk), fayalite (Fa), ilmenite (Ilm), silica (Sil), and symplectite (Sym). Fig. 1B inset BSE image of symplectite with dark silica, gray hedenbergite, and bright fayalite (mag. 700x, image used for modal analysis).

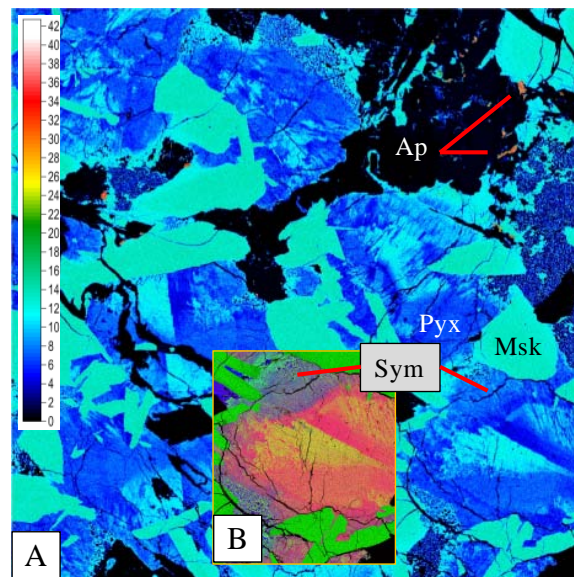


Figure 2A Ca quantitative map with weight % Ca scale (1024x1024 at 7  $\mu\text{m}$  per pixel). Apatite (Ap) is red-white. 2B inset RGB x-ray intensity map for pyroxene from lower right of 2A (red Mg K $\alpha$ , green Ca K $\alpha$ , blue Fe K $\alpha$ ). Symplectite (Sym) is lower in Mg and Ca compared to pyroxene.

#### References:

- [1] Zeigler et al. (2007) LPS XXXVIII (2005), #2110. [2] Liu, Y. et al. (2009) Met. Planet. Sci. 44, 2, 261-284. [3] Lindsley et al. (1972) Lunar Sci. 3, 483-485. [4] Carpenter et al. (2010) LPS XLI (2010), #2656.