ADVANCES IN ELECTRON-PROBE MICROANALYSIS AND COMPOSITIONAL MAPPING: APPLICATIONS TO LUNAR SAMPLES. P. K. Carpenter[1], R. A. Zeigler[1], B. L. Jolliff[1], E. P. Vicenzi[2], J. M. Davis[3], and J. J. Donovan[4]. Dept. Earth and Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University in St. Louis, Campus Box 1169, Saint Louis, MO, 63130 (paulc@levee.wustl.edu), [2]Smithsonian Institution, Museum Conservation Institute, Suitland, MD 20746; [3]Microanalysis Research Group, National Institute of Standards and Technology, Gaithersburg, MD, [4]Camcor, 1241 University of Oregon, Eugene, OR 97403.

Introduction: Advances in instrumentation and analytical techniques using electron-probe microanalysis (EPMA), and microbeam X-ray fluorescence spectrometry (µXRF) have been applied to the study of lunar samples. These techniques provide compositional information from discrete spots and in digital mapping mode, over a range of spatial resolutions that is appropriate for micro and macroscopic analysis of complex mineral chemistry and textures. We have applied ongoing research and development of EPMA and µXRF algorithms in simulation and analysis software, defocused-beam analysis (DBA), and hyperspectral-imaging techniques to study lunar samples.

Improvements in Quantitative X-ray Analysis: Improvements in EPMA and µXRF instrumentation has enabled large-scale X-ray mapping of lunar samples. The advent of silicon-drift (SDD) energy-dispersive (EDS) detectors with high-throughput digital pulse processing electronics has dramatically decreased mapping acquisition times and increased sensitivity. EPMA provides a relatively high spatial resolution of ~1 µm and allows sampling of up to 50-100 µm spot in defocused-beam analysis (DBA), and can analyze a wide range of elements including low energy X-rays, but trace element detection is ultimately limited by continuum X-ray production. Analysis by µXRF typically uses a minimum spot size of 50-100 µm, has superior trace element sensitivity and can be used on materials which are not vacuum compatible or exhibit electron-beam damage in the microprobe, but requires thicker samples for analysis due to X-ray penetration and has relatively poor low energy X-ray sensitivity. The two techniques are complimentary for these reasons.

EPMA has seen improvements in $\Phi(\rho z)$ algorithms and more accurate sets of mass absorption coefficients have improved quantitative analysis by both techniques. Quantitative EPMA corrects for atomic number (Z) effects of electron scattering and retardation during X-ray generation, absorption (A) of X-rays in the sample along the path to the detector, and fluorescence (F) of X-rays by both characteristic and continuum X-rays. The k-ratio is the measured X-ray intensity in the sample relative to that in the standard, and the calculated concentration C is determined by iterative calculation from C = k * ZAF. This iterative correction implicitly requires knowledge of the concentration of all elements in the sample volume and their effect on the element of interest. The

Bence-Albee α-factor algorithm utilized a hyperbolic relationship between measured X-ray intensity and calculated composition, and was used on earlier instruments for reasons of memory storage and execution speed. Constant term α-factors were calculated from a ZAF algorithm and measured concentrations were calculated relative to oxides which presented problems for analysis of metals. The accuracy of the constant term α-factor algorithm is known to be deficient, and a polynomial formulation has been used to generate α-factors which duplicate $\Phi(\rho z)$ algorithms and can be used for simple and rapid correction of simulated analysis problems and X-ray compositional map data [1]. The polynomial α-factor algorithm is referenced to pure element intensities and thus permits analysis of metals, sulfides, oxides, and silicates.

Analysis of Multiphase Sample Volumes: Mapping and spot analysis of multiphase materials results in excitation of a volume containing multiple phases, and accurate analysis must correct for X-ray generation and emission from discrete mineral phases rather than treating the volume as a homogeneous single phase. With reference to analysis of homogeneous materials, it is necessary to know the phase composition for iterative correction, and the phase density for conversion from sampled area fraction to weight fraction of the phase. Omission of a density conversion introduces significant errors in the analysis [2]. In DBA the contribution from each discrete phase is included as a weight fraction term in the iteration loop, and requires either explicit knowledge of the mineral chemistry or an approximation using a CIPW normative mineral calculation. The DBA technique and errors inherent in the calculation have been discussed previously [3-7].

Several problems exist in the general analysis of multiphase volumes. For phase mixtures with a grain size larger than the electron scattering volume (i.e., larger than 10 µm) the treatment of discrete phases is essentially identical for EPMA and µXRF because the sample must be deconvolved into the constituent phases for correction. The role of electron scattering from one phase to another is dimensionally secondary. For mixtures with a grain size that is smaller than the scattering volume (i.e., less than ~1 µm), or for grain geometries that include inclined and shallow boundaries, the role of differential electron backscattering is more important. For example, analysis of agglutinates containing nm to

μm-sized metallic Fe enclosed by silicates will exhibit enhanced X-ray production in the silicates due to differential electron backscattering from the Fe particles. For samples with a grain size significantly smaller than the scattering volume, the sample approximates a homogeneous material and no correction for multiple phases is necessary.

In the case of μXRF analysis, the area of electron scattering is replaced with a larger X-ray generation cross section, also known as the lateral sampling area. The production of X-rays depends both on the nature of the incident beam and on the atomic matrix of the material. In many samples, the primary fluorescing X-rays penetrate between 30 and 100 μm before becoming fully attenuated, and can produce lateral sampling areas as much as twice the incident beam area. Current research has focused primarily on characterizing macro phases larger than the incident beam. Such methods require quantification and refinement using the fundamental parameters algorithm [8].

To date, lunar samples and chondrules have been used almost exclusively as the test case for DBA accuracy, and no systematic analysis of physical mixtures of microanalysis standards has been conducted. The accuracy of DBA analysis on these natural materials was confirmed by comparison to bulk analysis which clearly did not utilize exactly the same material. Finally, algorithms for analysis of multiphase samples have stagnated at the research stage, are not widely available, and therefore have not been incorporated into existing analysis systems for EPMA and μXRF.

A polynomial α-factor formulation has been utilized in an Excel VBA interface designed to simulate X-ray production and emission from multiphase samples in support of DBA data correction. An example of analysis of a sample comprised of equal area fractions of anorthite and an $En_{80}Fs_{20}$ pyroxene are shown in Table 1. The ideal weight percent analysis was calculated from the known area fraction and density values for the two phases. The k-ratios for anorthite and the pyroxene were assumed to vary linearly with area and were input in the DBA correction using the ZAF factors for anorthite and pyroxene. The k-ratio data was also used to calculate an analysis for an assumed homogeneous sample. Disagreement of both the DBA and homogeneous correction with the ideal analysis suggest that the assumption of linear X-ray emission with area may not be fully justified, and that the densities used for calculation of the ideal analysis are not compatible with the atomic number component of the ZAF correction.

These and other software tools for simulation of electron scattering and X-ray production via Monte Carlo and Φ(ρz) algorithms used for bulk and thin-film sample geometries allow for complimentary analysis of multiphase samples. We are applying these tools to the analysis of lunar and martian meteorites as part of ongoing research that combines microanalysis with an evaluation of local and overall bulk chemistry and mineralogy [9-10].

Table 1.

	An ZAF	En_{80} ZAF	K-el 50:50AF	1	2	3
Mg	1.414	1.486	0.0613	10.57	8.88	8.61
Al	1.262	1.553	0.0768	8.15	9.45	10.45
Si	1.322	1.318	0.1762	23.74	22.67	22.64
Ca	1.089	1.090	0.0662	6.05	7.02	6.98
Fe	1.191	1.180	0.0443	6.07	5.10	5.10
O	3.045	1.874	0.1956	45.42	46.88	46.22

Key: *An and En80 ZAF*: Combined ZAF factor relative to pure elements for anorthite and $En_{80}Fs_{20}$ pyroxene. Note large difference for Al Kα and O Kα correction. All values calculated using polynomial α-factor algorithm based on Armstrong Φ(ρz) algorithm and Henke mass absorption coefficients.

K-el 50:50 AF: Calculated emitted X-ray intensity relative to pure element for a sample with 50:50 area fraction using k-ratio for anorthite and En_{80}.

1. Ideal weight percent element analysis for 50:50 area fraction anorthite – En_{80} sample converted to weight percent using ρ = 2.76 for anorthite and ρ = 3.81 for En_{80}.

2. Analysis obtained using k-ratios from 50:50 area fraction and ZAF factors for anorthite and En_{80}. This is a normalized DBA correction.

3. Analysis obtained using k-ratios from 50:50 area fraction and assumption of homogeneous sample.

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