Large-Area, Stage-Rastered WDS X-Ray Mapping in Electron Probe Microanalysis

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INTRODUCTION
An X-ray map is a compositional image that shows the distribution of an element on the surface of a sample. It can be acquired using a wavelength- or energy-dispersive spectrometer (WDS or EDS) by the movement of an electron beam on a sample surface in an electron probe microanalyzer (EMPA) [1-5].

Electron beam-rastered WDS X-ray maps of large surface areas are often defocused near the edges due to the loss of X-ray intensity when the scanning electron beam strays away from the vertical [6,7]. Therefore, the stage-rastered method is preferred in acquiring large area WDS X-ray maps. In this method, the electron beam is fixed while the stage is moved in order to expose the specimen surface to the electron beam to be imaged. Large-area, low-magnification X-ray maps provide a means to estimate proportions of the different components (e.g. phases or compounds) and to determine the chemical and spatial relationships between the components of a composite sample [8-10].

These maps have been used to determine the composition of a fine-grained matrix of a rock that was difficult to analyze by other techniques [9]. Spatial relationships, shedding light on the mode of formation of the constituent phases, may be determined through image analysis based on a pixel counting technique [10]. The purpose of this article is to elaborate the methods described in these earlier papers.

MATERIALS AND METHODS
Rock samples were cut and polished first with coarse SC paper and then with alumina grit of different sizes, the final grit size being 0.06 µm. The samples were then cleaned in an ultrasonic cleaner, air dried, and coated with a 25-nm thick film of graphite in a vacuum carbon evaporator.

Sets of large-area backscattered electron (BE) image and X-ray maps were acquired by the stage-rastering method with a JEOJXA-733 Superprobe equipped with five WD spectrometers. The Si, Al and Mg maps were acquired with thallium acid phthalate (TAP), Fe with lithium fluoride (LIF), and Ca with pentaerythritol (PET) analyzing crystals. Image resolutions were between 20 and 40 µm. The dwell-time, the time spent by the beam on each point where an X-ray measurement is made, was typically 30 milliseconds per point. The beam current and accelerating voltage were 30 nA and 15 kV, respectively. Image acquisition time was higher for higher resolutions or larger areas (i.e. more points measured along each line) or longer dwell times. The hardware (stage motors) speed limit for the stage was 2 mm sec⁻¹. The average stage speed to acquire a 15 mm × 30 mm image at 20 µm resolution was about 0.7 mm sec⁻¹, resulting in an acquisition time of about 14 hours.

The area percentage of each sample component (e.g. phase, matrix) was calculated from the X-ray maps and the unknown chemical composition of the matrix was determined based on the X-ray maps and a large-area backscattered electron (BE) image of a Hawaiian lava sample. (A) Backscattered electron (BE) image. (B) Mg WDS X-ray map. (C) Ca WDS X-ray map. The imaged area is 15 mm x 30 mm.

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BIOGRAPHY
Nilanjan Chatterjee obtained his PhD in geochemistry from the City University of New York in 1989. He has 17 years of experience working with electron probe microanalysis at the American Museum of Natural History, New York, the University of Kentucky, and since 1993 at MIT, studying a wide variety of material including rocks, meteorites, ceramics, metals and archeological samples. He has co-authored 22 papers and 26 meeting abstracts.

ABSTRACT
An electron probe microanalyzer equipped for wavelength-dispersive spectrometry can be used to obtain a set of large-area elemental X-ray maps of composite samples by moving the sample stage and keeping the electron beam stationary. These maps may be used in phase (compound) identification, phase proportion and bulk chemical composition determinations and studying interphase chemical and spatial relationships. The composition of a phase, difficult to analyze by conventional techniques, can be determined through a mass-balancing method. Spatial relationships can be determined by comparison with a simulated image having the same phase proportions but random position of phases through a pixel counting technique.

KEYWORDS
scanning electron microscopy, X-ray microanalysis, electron probe microanalysis, X-ray mapping, wavelength-dispersive spectrometry, stage-rastered image, image analysis, bulk composition

Figure 1: Large-area, stage-rastered images of a Hawaiian lava sample. (A) Backscattered electron (BE) image. (B) Mg WDS X-ray map. (C) Ca WDS X-ray map. The imaged area is 15 mm x 30 mm.
from mass-balancing equations such as $$w_i \text{SiO}_2 = w_i \text{SiO}_2^{\text{matrix}} + w_i \text{SiO}_2^{\text{phases}}$$ where $w_i$, the mass of component $i$, is given by $\text{(area\%)}_i \times \text{(density)}_i$, and $\text{SiO}_2^{\text{matrix}}$ was determined from inductively coupled plasma measurements and the values for $\text{SiO}_2^{\text{phases}}$ were determined by conventional EPMA spot analysis techniques. Similar equations were used to calculate the amount of the other oxides in the matrix.

To determine spatial relationships by the pixel counting method, image analysis began by considering a large square-shaped area of the image. The number of pixels covered by each phase inside the area was counted and the result was plotted in a triangular diagram with the three main phases at the three corners. Samples with more phases would require more complex plotting methods. The area-proportion (i.e. the abundance) of the phases in the square constrains the position of the point in the diagram. The large square was then divided into four equal squares and the procedure was repeated on each square. Each square was again subdivided into four equal but smaller squares and the procedure was again repeated. This process was repeated until each square contained only one pixel. In the triangular diagram, squares containing only two phases plotted on a side of the triangle and squares containing only one phase plotted on one of the corners. For the smallest square size of one pixel, each square contained only one phase and all the squares plotted on the corners. The number of one-pixel squares plotting on each corner in the final step is also constrained by the area proportion of the corresponding phase in the original image. The spatial association of a phase pair requires that a large number of points plot on the side of the triangle containing the two phases.

Next, the same analysis procedure was repeated on a computer-simulated image that contained the same phase proportions but the positions of the phase grains were random. Since the average grain size of the different phases was different, the image was simulated in steps adjusting for the grain size and phase proportions of the remaining material. The number of points plotting on each side of the triangular diagram for the simulated image was compared with the number of points on the same side of the triangle for the actual image. If a side of the triangle for the actual image contained significantly more points than the corresponding side of the triangle for the simulated image, it was concluded that the corresponding phase pair was spatially associated in the sample.

**RESULTS**

Figure 1 shows large-area, stage-rastered BE image and Mg and Ca WDS X-ray maps of a sample of Hawaiian basaltic lava collected from the flank of the Haleakala volcano on East Maui, Hawaii [9]. The sample consisted of large crystals of the minerals olivine and augite embedded in a matrix that was originally glassy, but later crystallized to minute crystals of olivine and augite. Figure 2 shows only the large olivine and augite crystals isolated from the Mg and Ca X-ray maps, respectively, following image manipulation. The area percentages of large olivine and augite crystals and the matrix calculated from these images are shown in the top row of the table inset in Figure 2, which also shows the matrix composition calculated from the mass-balancing equations. The errors resulted from the variations in olivine and augite composition as determined by conventional EPMA.

Figure 3A–E show large-area, stage-rastered BE and S, Al, Fe and Mg WDS X-ray maps of a mantle xenolith sample from South Africa [11]. This sample primarily consisted of three minerals: olivine, orthopyroxene and garnet. The minor occurrence of clinopyroxene was considered insignificant for the purpose of this demonstration. The X-ray maps were combined into a single digitized image that shows the different mineral components (Figure 3F).

**DISCUSSION**

The partitioning of elements between the large crystals and the fine-grained matrix of the Hawaiian lava sample is sensitive to the pressure and temperature conditions of the environment from which the lava originated. To estimate these conditions, it was necessary to determine the chemical composition of the fine-grained matrix [9]. Several different techniques may be used to determine the chemical composition of the matrix. One of these, EPMA spot analysis with a defocused beam, gave highly variable results because of the heterogeneity in the matrix. Determining the
matrix composition by separating the large crystals from the bulk sample is a very difficult and tedious process. A mass-balancing approach using the large-area X-ray maps provided good results.

The BE image (Figure 1A) does not have enough contrast to be useful in determining the area proportion of the mineral components. Since augite (Ca(Mg,Fe)SiO$_3$) contains Ca in addition to the elements present in olivine ([Mg,Fe$_2$SiO$_4$]), Mg and Ca X-ray maps (Figure 1B, C) are more diagnostic. Olivine appears lighter than augite in the Mg X-ray map because olivine contains more Mg. In the Ca X-ray map, however, olivine appears dark. In the mass-balance equation, the density of the matrix was assumed the same as the density of the bulk sample. This is not unreasonable because the matrix is composed of the same minerals as the bulk, i.e., fine crystals of olivine and augite. If the density of the matrix were very different from that of the bulk sample, a more rigorous iterative approach would be required to solve the mass-balancing equations.

Mantle xenoliths are pieces of the Earth's mantle that were transported to the Earth's surface after being entrapped in kimberlitic magma. The samples in this study are from the Jagersfontein and Kimberley regions of South Africa [11]. The spatial associations of the different minerals in the mantle xenoliths provide important information about their origin [10]. Spatial associations may be obvious in some samples. For example, garnet always exists at the rim of pyroxene in one of the samples (Figure 6A). In other samples, the relationships are not obvious (Figure 6B). In such samples, the pixel counting technique was used to determine mineral-pair spatial associations.

The BE image and the Si, Al, Fe and Mg X-ray maps (Figure 3B-E), if considered separately, are not very useful in phase identification. Hence, the X-ray maps were combined into a single digitized image that clearly identifies the different minerals (Figure 3F). The pixel counting procedure is demonstrated in Figure 4. The images on the left side of Figure 4 show the number of squares considered in each step, whereas the triangles on the right show the points where the composition of the squares plot in an olivine-orthopyroxene-garnet ternary diagram. In the first step, the position of the point in the ternary diagram is constrained by the area proportion of the three minerals. In subsequent steps, the points migrate toward the sides or the corners of the ternary plot. In the last step, all the squares, each containing only one pixel, plot on the corners (Figure 4J). The number of one-pixel squares plotting on each corner in the final step is also constrained by the proportion of the mineral representing that corner. Comparing the results from the image of Figure 3F and a simulated image (such as Figure 5B), it was concluded that garnet is spatially associated with orthopyroxene and formed from orthopyroxene in response to a change in pressure-temperature conditions as the xenolith was brought to the Earth's surface.

CONCLUSIONS

A set of useful large-area, stage-rastered WDS X-ray maps showing elemental distributions in a polished sample can be obtained overnight with an electron probe microanalyzer. Large-area X-ray maps can be used for estimating phase proportions and bulk composition. Compositional maps of a difficult-to-analyze phase or sample component may be accurately determined using mass-balancing equations.

Combined elemental X-ray maps may be better for mineral identification than individual images. An image can be analyzed step-by-step by counting pixels for each phase and by comparing with a simulated image, with the same phase proportions but random position of the phases, to determine if phase pairs are spatially related.

REFERENCES

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Figure 4: Results of the pixel counting technique. See Figure 3 for mineral color codes. Ortho- and clinopyroxene have been considered as one phase for this analysis. (A) Analysis started on a square image area. (B) Pixel counts of the square plotted in a triangular diagram. (C) Initial square divided into four squares and plotted in (D), (E-I) Intermediate steps. (J) Final step showing all squares plotting at corners.