ELECTRON MICROPROBE ANALYSIS IN 21ST-CENTURY ARCHAEOLOGY:
ITS STRENGTHS, ITS WEAKNESSES, AND THE ADVANCEMENTS USEFUL TO ARCHAEOLOGISTS

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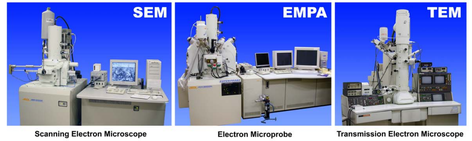
Electron Microprobe Laboratory

I. Abstract

Electron microprobe analysis (EMPA), also called electron probe microanalysis, is an analytical technique used to establish the chemical composition of small areas on specimens. Additionally, the instrument can function much like a scanning electron microscope (SEM) and acquire highly magnified images of specimens. EMPA is quite versatile and a dominant analytical technique in the geosciences. The technique was developed in the 1940s and 1950s, and soon archaeologists were considering its usefulness. Early archaeological applications involved analysis of layered materials (paints, glazes, metal surface alteration) and mixtures (identifying particles in metals, ceramics, glasses). These early studies recognized that EMPA is well suited to heterogeneous materials. This detail, though, has been overlooked in some recent archaeological descriptions of EMPA, creating confusion about its strengths. Other techniques have recently become more popular in archaeology, and EMPA is sometimes considered "old news." Just as a 1960s TV set differs greatly from the new high-definition model, modern instruments make EMPA more useful to archaeologists than ever before. Recent advancements in digital imaging and automation will be advantageous to archaeological researchers. Archaeological examples, including geological and human-made materials, show EMPA's advantages and strengths.

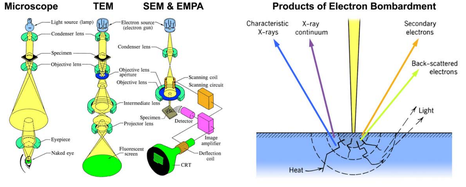
II. What is Electron Microprobe Analysis?

Electron microprobe analysis (EMPA), also called electron probe microanalysis, is an analytical technique that is used to establish the composition of small areas on specimens. The electron microprobe is one of three main types of electron microscopes, as shown below:



Scanning Electron Microscope | Electron Microprobe | Transmission Electron Microscope

As in all forms of electron microscopy, EMPA involves bombardment of the sample with a beam of accelerated electrons. The electron beam is focused on the surface of the specimen using a series of electromagnetic lenses. For SEMs and electron microprobes, an image is formed in a different way than in visible-light microscopes and TEMs. The beam of electrons does not pass through the sample to form an image. Instead the focused beam is scanned across an area on the sample surface (below left illustration). As the electrons interact with the sample, there are various products (below right illustration), including two different types of electron signals used for imaging: secondary electrons (SEs) and backscattered electrons (BSEs). SE images provide topographic information; these images are the kind typically associated with SEMs (e.g., highly magnified spider eyes or salt crystals). BSE images show contrast among areas with different compositions; areas with a high mean atomic number appear bright.



The beam of energetic electrons also produces characteristic X-rays within a very small volume of material (commonly a few cubic microns) just below the sample's surface. Every element on the periodic table (except H and He) emits a specific set of X-rays under electron bombardment. Measuring the X-rays indicates which elements are present and their concentrations. Electron microprobes have two systems to detect characteristic X-rays. One detector system measures the X-ray wavelengths (WDS), and the other measures their energies (EDS). The two systems are discussed in cross-section callouts in the center of the poster. Electron imaging allows one to select specific areas on a sample for analysis. EMPA analyzes spots as small as one micron in diameter (high spatial resolution), and the process is not destructive to a sample.

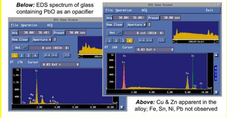
Wavelength-Dispersive Spectrometry (WDS)

Used for quantitative analysis and element maps; "tunes in" X-rays by wavelength for clear element separation (fewer overlaps) and detection limits superior to EDS

Quantitative analysis of two volcanic glass samples; totals show relative error <±0.5%

Energy-Dispersive Spectrometry (EDS)

Collects an entire spectrum at once, so the full periodic table is visible with the click of the mouse and in seconds; suffers from peak overlaps and worse detection limits

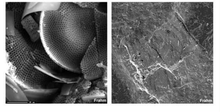


Below: EDS spectrum of glass containing PbO as an opacifier

Above: Cu & Zn apparent in the alloy; Fe, Sn, Ni, Pb not observed

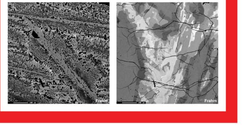
Secondary-Electron (SE) Imaging

Shows topographic information about the sample; type of image usually associated with SEMs; *left:* fossil diatoms; *right:* tiny feldspar crystal on a dacite flake surface



Backscattered-Electron (BSE) Imaging

Shows compositonal contrast; areas with high mean atomic number appear brighter; *below:* two metallic slags differ in structure due to two different smelting techniques



III. Strengths and Weaknesses of EMPA

The electron microprobe is a versatile tool, but like all analytical techniques, it is not the solution to all issues of chemical composition. EMPA has both its strengths and weaknesses:

Strengths

High spatial resolution • High precision (<1% relative error) • All elements except H, He, and Li measurable • Low detection limits (100 ppm or less) • Measurements take a minute or two

Weaknesses

Isotope ratios cannot be measured • Minerals with the same composition but different crystal structures cannot be easily differentiated • Complex organic molecules not readily analyzed

IV. Technological Advances in EMPA

Raymond Castaing assembled the first microprobe in 1948, and the first commercial instrument was introduced in 1958. Just as televisions have significantly improved in the last fifty years, so too have microprobes. Automation advancements have been considerable, and new computers permit nearly real-time data processing and unattended operation. Innovations include: electron gun advancements that allow high-resolution analyses, digital maps, mapping irregular surfaces, fully automated particle identification and analysis, and live element imaging.

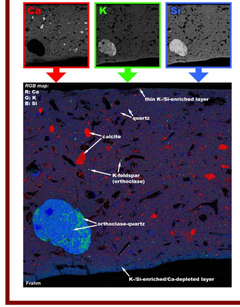
V. Select Early Applications: The First Thirty Years

1958: R.W. Smith thinks EMPA can establish area-period composition norms for ancient glass.
1960: G. Roberts reports a microprobe was being installed in Oxford's archaeological labs and that the new instrument would first be used to study surface enrichment in metal artifacts.
1963: A.P. Hornblower explains the Oxford microprobe was used to analyze coloring agents of a Chinese lacquer box, paint of a 16th-century Dutch painting, and a bronze pin.
1966: A.O. Shepard used EMPA to show the manganese used to source sherds to Cuicuilco or Teotihuacan occured in natural inclusions within the clay, not in added temper.
1968: J.A. Charles studied silver capping on copper rivets that attached the handle to a bronze Minoan dagger; the interface between the metals showed how they were bonded.
1969: R. Giovanoli studied Roman mural paintings; EMPA showed that murals from two areas had layers with different compositions, proving there were two distinct mural techniques.
1972: J.A. Charles studied the manufacturing techniques of southeast European copper axes.
1979: Kamilli and Lamberg-Karlovsky analyzed ceramic ware styles from Tepe Yahya, Iran to ascertain if the styles also reflected material and technological variations.
1982: I.C. Freestone discusses the application of EMPA to examine clays, slips, and glazes as well as the determination of provenance and firing temperature.
1984: Merrick and Brown analyzed obsidian artifacts from four archaeological sites in Kenya.
1985: Abbott and Schaller analyzed Hohokam pottery for evidence of exchange systems.
1988: Hallett et al. investigated materials and methods used to decorate ten types of medieval Islamic ceramics from North Yemen and concluded an intricate ceramic industry existed.

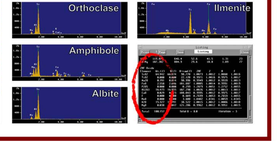
VI. Early Applications & Recent Descriptions

These and other early archaeological applications involved analysis of layered materials (paints, glazes, metal surface alteration) and mixtures (identifying particles in metals, ceramics, glasses). Such studies recognized EMPA is especially well suited to heterogeneous materials. This detail, though, has been overlooked in some recent descriptions of EMPA, creating confusion about its advantages. For instance, Kempe and Templeman (1983) assert its "most likely use is perhaps for chemically and mineralogically homogeneous rocks like... the flint-chert-jasper group" in *The Petrology of Archaeological Artefacts* (46). Andrefsky (1998) repeats their claim and states that it "is best used on chemically and mineralogically homogeneous rocks" (42). These statements are misleading. EMPA is a spot analytical technique, meaning chemical information is collected from only a small volume, not the entire sample. For a perfectly homogeneous substance, spot analyses would be representative of the whole. Flint is rather homogeneous compared to most rocks, so Kempe and Templeman may have meant EMPA can provide its bulk composition. An advantage of EMPA, though, is the ability to show compositional variations within a sample and analyze its separate components. It is also possible that Kempe and Templeman meant EMPA can investigate the silica matrix of flint and any small mineral inclusions separately. Either way, the statement is unclear. If such ambiguous statements continue to be repeated, this confusion about the advantages of EMPA will proliferate. The examples that follow intend to show suitable archaeological applications of spot X-ray analysis and scanning electron microscopy.

VII. Ceramics - Example: Tell Mozan Wares

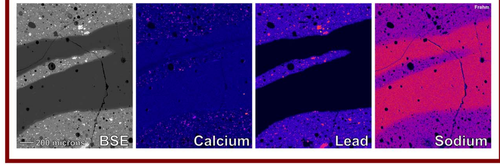


Ceramics are usually both mixtures (with naturally occurring inclusions and added temper in the clay) and layered materials (with slip, glaze, paints, and surface alteration), which means ceramics are well suited to EMPA. Shown is a sherd from Tell Mozan (ancient Urkesh) in NE Syria. Archaeologists want to learn if the ware styles correlate with differences in raw materials and manufacturing. *Left:* Element maps were combined to show some of the mineral inclusions and the surface alteration. *Below:* EDS spectra and WDS quantitative analyses were used to characterize further this particular ware.



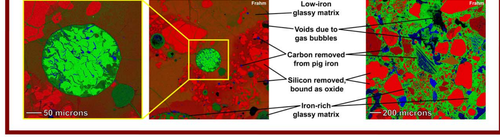
VIII. Glass - Example: East Java Mosiac Beads

East Java mosiac beads are not only found in Java but also Malaysia, the Philippines, Sumatra, and Kilimantan. These beads are among the heirloom items on Palau and were used as a form of currency. Their manufacture and raw materials are subjects of interest. The BSE image and element maps below show the interface between two glasses. One glass used lead oxide as an opacifier, and the two glasses differed in their soda (Na) and lime (Ca) contents.



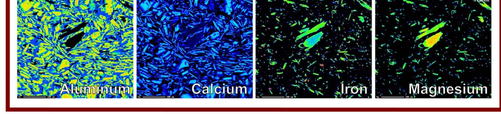
IX. Metallurgy - Example: Historical Iron Slag

The Elliot Park Neighborhood Archaeology Project involves the excavation of a historic site near downtown Minneapolis. Maps indicate the area was a residential neighborhood in the mid-19th century. Excavators were surprised to find some slag and had no idea what type it was. EMPA revealed it was slag from a puddling furnace. Puddling is a process used to make wrought iron from pig iron by removing excess carbon, silicon, and other impurities. The process causes loss of iron to the slag, so the glassy matrix of the slag is iron-rich. Below are element maps in which iron content is displayed in shades of green, carbon in blue, and silicon in red.



X. Lithics - Example: Japanese Sanukite Stone Tools

EMPA is a dominant analytical technique in geology because it permits the analysis of individual minerals *in situ*. Rocks are mixtures of minerals, so a bulk technique can provide no information about the distribution of elements among the minerals. One possible approach to sourcing lithic materials is to take a more geological approach and consider the minerals individually. Sanukite is a stone that comprises as much as 90% of lithic assemblages in Japan. It has a glassy matrix and two major minerals: orthopyroxene (magnesium iron silicate; green in the Mg and Fe maps) and andesine (sodium calcium aluminum silicate; light blue in the Ca map). Trace elements can be found and measured in the minerals which contain them. Then, using petrographic methods from geology, rock compositions and structures can be used to characterize sources.



XI. Acknowledgments

Electron microprobe analyses were carried out at the Electron Microprobe Laboratory, Department of Geology and Geophysics, University of Minnesota-Twin Cities; probelab.geo.umn.edu. Aid in sample preparation was provided by lab assistants of the Electron Microprobe Laboratory: Travis Tenner, Meagan Thompson, and Samantha Heck. The illustrations in Section II are based on figures from JEOL and McKinley (1964), respectively, and the three photographs of electron microscopes came from the website of the National Institute for Materials Science in Japan. In Section IV, the electron microprobe photographs are from JEOL, the modern television from Sony's website, and the older television set from the TV History website. The central cutaway by the author is based on several diagrams in JEOL literature and manuals. The slag sample came from the Elliot Park Neighborhood Archaeology Project (principal investigators: Kent Bakken and Patricia Emerson). The ceramic sample was provided by the International Institute for Mesopotamian Area Studies (principal investigators: Giorgio Buccellati and Marilyn Kelly-Buccellati) and was generously approved for export and study by the Directorate General of Antiquities and Museums of the Syrian Arab Republic. This poster benefited greatly from comments by Penny Frahm, a doctoral student in science education. It is also a pleasure to acknowledge the guidance and mentorship of Dr. Peter McSwiggen, who taught me to use the electron microprobe and put me to work in the lab, and of Professor George "Rip" Rapp, who has championed my geoarchaeological studies and research over the years.