

A thermal field-emission electron probe microanalyzer for improved analytical spatial resolution

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INTRODUCTION

Electron probe microanalyzers (EPMA – also referred to as electron microprobes) have historically been the premier instruments for microanalysis, because of their precision, stability and reproducibility. Their spatial analytical range was typically on the order of a couple of micrometers, using either a tungsten filament or a LaB₆ crystal for their electron source. However, researchers now have much more demanding requirements and need to be able to both map and quantitatively analyze features that are on the sub-micrometer scale. This has historically been outside of the range accessible by EPMA, limited by its electron beam diameter and inability to work at low accelerating voltages.

This changed with the advent of a thermal field-emission gun that could work on the EPMA. Cold field-emission electron guns (CFEG) became available in the late 1980s and have been embraced for use in scanning electron microscopes ever since. However the CFEG has very low beam currents and poor beam stability. These two limiting factors made them unsuitable for the EPMA, which depends on both high beam current to produce sufficient X-rays for analysis, and good beam stability for reliable quantification and long term mapping.

The development of the Schottky thermal field-emission gun (TFEG) now makes possible a field-emission EPMA. The Schottky emitter runs at a significantly higher temperature than the CFEG, producing a more stable electron beam by minimizing the amount of gas-absorbed onto the tip. However, the TFEG still produces an electron beam much smaller and brighter than that of the tungsten filament gun, and much more stable and with a much higher beam current than the CFEG. This highly stable, very bright, electron beam, with a very high emission current, has made the field-emission gun a viable option for electron probe microanalyzers, and as a result has dramatically improved the spatial resolution of microanalysis.

The JEOL JXA-8530F field-emission electron microprobe offers two additional, critical features in their gun and column that make it practical to add the field emission to the electron microprobe.

(1) In Lens Thermal FEG – By lowering the FE-gun into the top of the condenser lens, a huge increase in beam current has been achieved. A typical JEOL FE-EPMA can now achieve up to 1 microamp of beam current.

(2) Aperture Angle Control Lens – This new lens continuously adjusts the aperture angle of the beam. This optimization of the aperture angle is done to achieve the smallest possible spot size for every beam current and accelerating voltage.

IN LENS THERMAL FEG

A Schottky thermal field-emission electron gun is capable of producing very high emission currents. The next step is to turn those high emissions into a high beam current. To deliver the brightest beam, with the smallest diameter, at any accelerating voltage, the electron gun of the JEOL JXA-8530F is placed within the upper electron field of the condenser lens (Figure 1). This funnels the electrons from the gun into a narrow angle, allowing many more to pass through the anode aperture, and subsequently to be focused by the objective lens into a very small beam with a beam current ten times higher than the conventional FEG system (200 nA guaranteed, but 1 μ A is typically achievable) [1]. This configuration delivers high beam currents for microanalyses, but also allows for the best imaging at low beam currents.

APERTURE ANGLE CONTROL LENS

In an ideal system, using the largest convergence angle for a beam would produce the smallest beam diameter. However in real columns, aberrations limit the beam diameters that can be achieved. As the aperture angle is increased, spherical aberration also increases, turning the sharp spot into a diffused region. For every accelerating

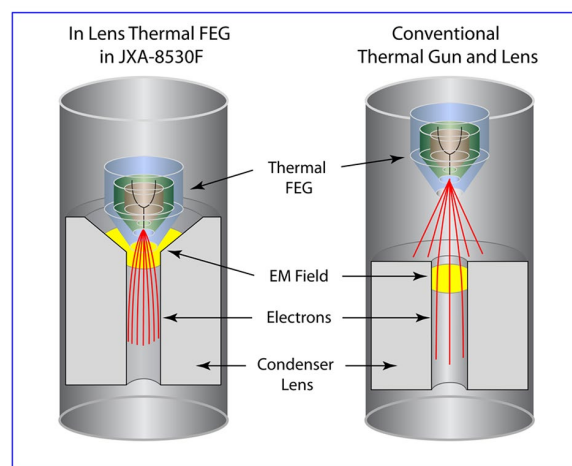


Figure 1

Comparison of the JEOL in-lens thermal FEG with a conventional thermal gun and lens. The in-lens FEG produces significantly higher beam currents.

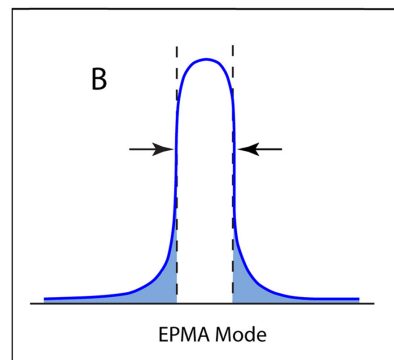
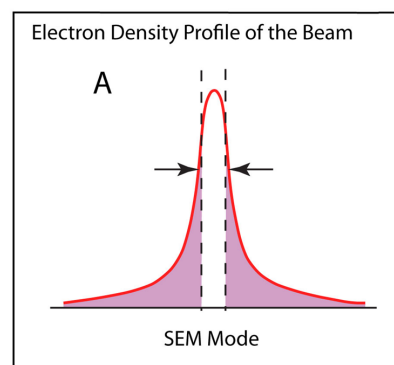


Figure 2

Comparison of the electron density distribution in the beam when optimized by the aperture angle control lens for low beam current imaging (A – SEM mode) versus high beam current microanalysis (B – EPMA mode).

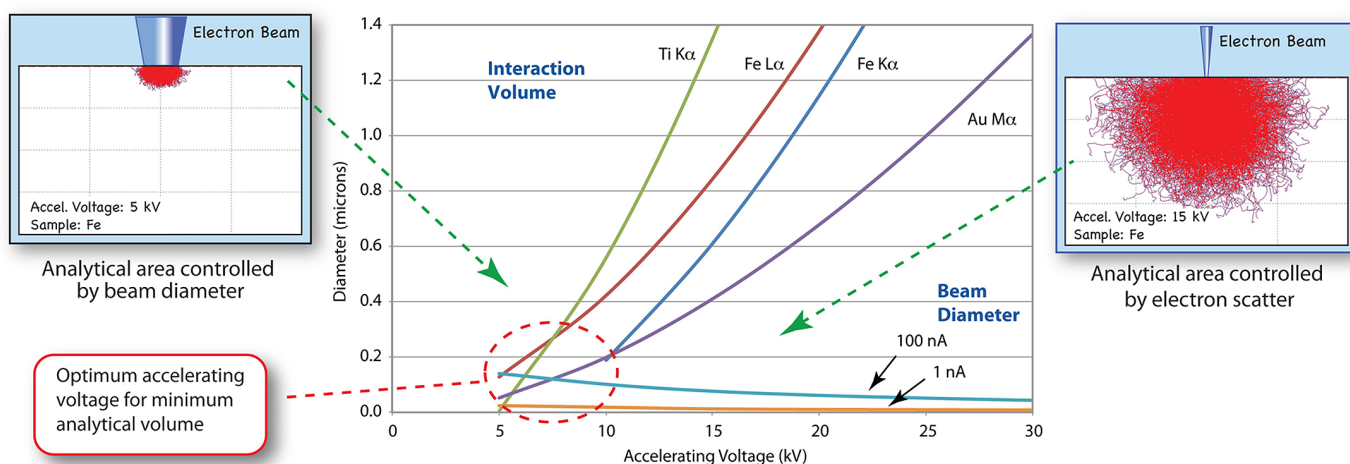


Figure 3

Minimizing the analytical area is a balance between the increase in the beam diameter and decrease in the electron scatter within the sample with a reduction in accelerating voltage. The beam diameter was measured on JEOL JXA-8530F field emission electron microprobe. Size of X-ray generation volume calculated from the Castaing equation [2] and Monte Carlo calculations of electron trajectories (e.g.[3]).

voltage and beam current setting, there is an optimum aperture angle that will produce the smallest spot size. JEOL utilizes an aperture angle control lens, positioned just above the objective lens, to automatically adjust the aperture angle to optimize it for each specific column condition.

When the aperture angle is optimized for low beam currents, the profile of the electron density in the beam has more of a V-shape (Figure 2a). The highest density region is very small, but there are significant tails that extend out from the center region. This is suitable for imaging, but not for analyses. The same electron beam profile at high beam currents would result in a very broad beam. Instead for high beam currents, the aperture angle is optimized to produce a more of a U-shaped electron density profile (Figure 2b). This puts more electrons into only a slightly broader electron beam, but greatly reduces the amount of beam spray outside of the core zone, something critical for high-resolution microanalyses.

LOW KV ANALYSES

A small electron-beam diameter does not necessarily mean a small analytical area. The size of the analytical area is controlled by both the size of the electron beam and the amount of electron scattering that takes place within the sample. The amount of scatter is controlled by the accelerating voltage and the average atomic number of the sample. Therefore a reduction in the accelerating voltage can be used to minimize the analytical area. No improvement in the analytical area is gained when analyzing at 15 or 20 kV, regardless of how small the beam diameter.

The optimum accelerating voltage is a trade-off between the beam diameter, which increases in size with decreasing accelerating voltage, and the electron scatter within the sample, which decreases with decreasing accelerating

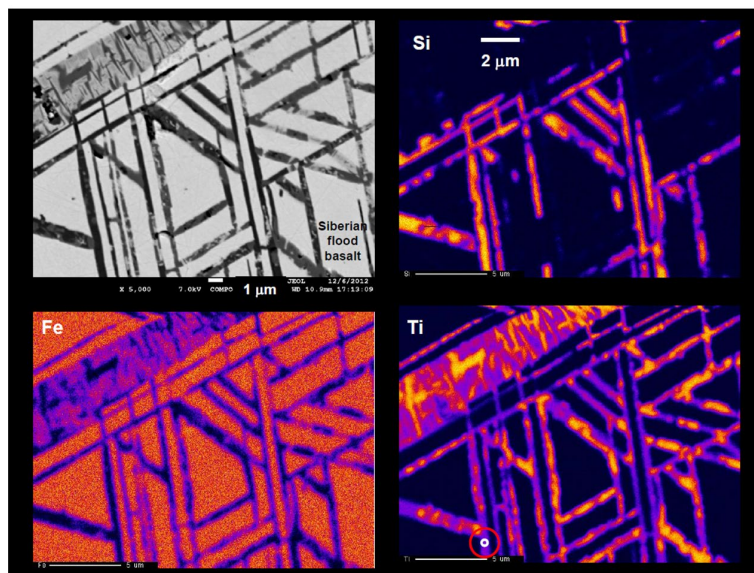


Figure 4

Backscattered electron image (scale bar = 1 μm) and X-ray maps (scale bar = 2 μm) of a rutile (TiO $_2$), titanite (CaTiSiO $_5$), titanomagnetite (Fe,Ti,Al-oxide) intergrowth in a polished section of the Ivakinsky (Siberian) flood basalt. The Ca X-ray distribution is identical to that shown for Si (upper right). We were able to perform quantitative analyses of each of the phases with an analytical resolution of <300 nm. For example, we were able to determine the composition of individual rutile crystals as small as 250 nm wide. We were also able to determine the accurate composition of these titanites, which contained minor amounts of Fe and Al, even when surrounded by Al-rich Fe-Ti-oxides. The images shown have a total area of 19.5 \times 26 μm .

voltage (Figure 3). Typically the minimum analytical area will occur at around 5-8 kV, depending on the material involved and the type of electron gun and column. At higher accelerating voltages, the electron scatter within the sample produces a larger analytical area. At lower accelerating voltages, the increased size of the beam diameter produces a larger analytical area.

APPLICATIONS AND PERFORMANCE TESTS

To test whether the theoretical advantages of a field-emission source in an electron microprobe actually result in significantly improved performance and extend the range of applications for small area mapping and quantitative analysis, we used the newly installed JEOL JXA-8530F at Arizona State University to perform analyses of sub-

micrometer areas in a series of geological specimens currently being studied at the Carnegie Institution of Washington. Specifically, we examined polished sections of earth rocks, meteorites and products of laboratory high pressure experiments to see: (1) how small are the features that can be accurately mapped and analyzed without contributions from the surrounding material in fine-grained intergrowths; and (2) how fine a scale can linescan analyses be performed at grain boundaries and in compositionally zoned materials.

Figure 4 shows a backscattered electron image and X-ray maps from a thin section of a volcanic rock that is part of the Siberian flood basalts thought to have played a significant role in the greatest mass extinction in earth history at the end of the Permian period (e.g. [4]). The amount and types of fluids present in these rocks during their eruption are

important in understanding the impact that they had on the environment at that time.

The compositions of finely intergrown Fe-Ti-Al-oxides and silicates as found in this section give important information regarding the fluids present during their formation. However, the individual intergrown laths and blebs have widths as small as 200 nm and thus cannot be analyzed by conventional electron microprobe techniques.

We performed quantitative analyses of larger crystals ($>1\ \mu\text{m}$) of the various phases at 7 keV and compared them to analyses of grains as small as 300 nm in diameter or width (the size of the white circle in the lower left area of the Ti X-ray map; the surrounding red circle is the size of the analytical area for a conventional microprobe at 15 keV, Figure 4). TiO_2 grains inside of titanite ($\sim\text{CaTiSiO}_5$) showed no Ca or Si, indicating no contribution from their surroundings. TiO_2 grains inside of Fe-Ti-Al-oxides showed no Al and the same levels of Fe at those surrounded by very low Fe-containing titanite (e.g. Figure 5). Titanites in contact with Al-rich Fe-Ti-oxides showed no excess Al compared with those surrounded by TiO_2 . As a result, we were able to accurately determine the Al and Fe contents of sub- μm grains of titanite and the Fe content of sub- μm TiO_2 grains.

Figure 6 shows X-ray maps from a very fine grained mixture of mineral grains and glass in a chondrule from the Semarkona meteorite. Chondrules are round objects that solidified from molten or partially molten droplets originally present in the solar nebula during the time that the meteorites' parent bodies were forming. They contain some of the oldest preserved material in our solar system. The Semarkona meteorite is one of the most unequilibrated (or least altered) meteorites that contain chondrules. As such, these objects are of particular interest – especially the differences in composition along grain boundaries and at the rims of the minerals.

The problem in studying this meteorite is that the grains and reaction rims are so fine-grained. The glass-mineral region shown in Figure 6 is an intimate mixture of K-Al-rich glass and quench crystals of pyroxene ($\text{Ca,Mg,Na}_{1.0}(\text{Mg,Fe,Al,Cr,Ti})_{1.0}(\text{Si,Al})_2\text{O}_6$ and olivine ($\text{Mg,Fe}_2\text{SiO}_4$) that is conventionally considered “too fine grained to be analyzed by electron microprobe analysis” [5]. As can be seen in the X-ray maps, we can clearly distinguish between the glass and silicate minerals and see evidence of sub- μm scale zonation at the rims of the mineral grains.

Figure 7 shows a linescan obtained at 7 keV across the boundary between the glass and an olivine grain in this section.

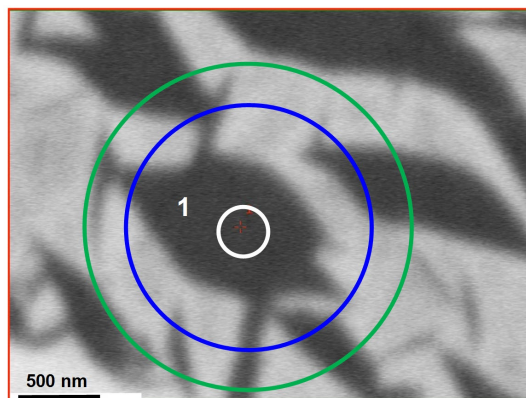


Figure 5 Backscattered electron image (scale bar = 500 nm) and analytical area (white circle, $\sim 300\ \text{nm}$) of a 600 nm diameter rutile grain surrounded by Fe-Ti-Al oxide. No Al was detected in the analysis of the grain at 7 keV and the 1.8 weight % of Fe detected was consistent with that measured in larger grains. The blue and green rings indicate the type of minimum analytical areas obtainable using conventional electron microprobes at 15 keV.

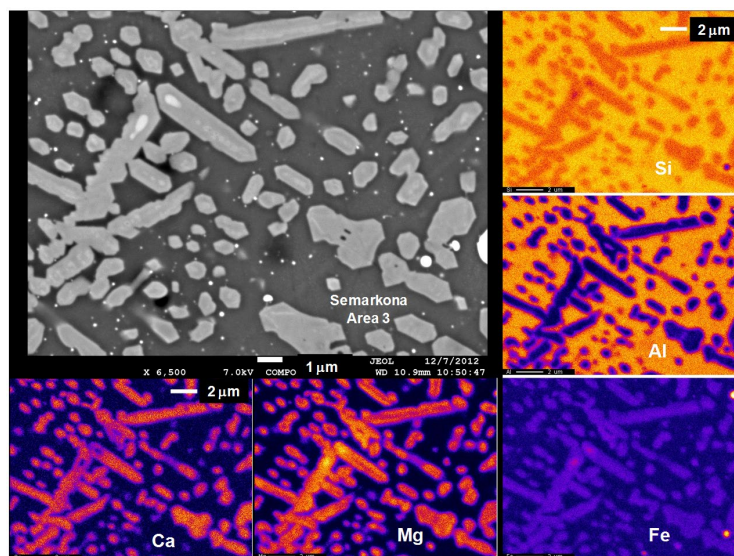


Figure 6 Backscattered electron image (scale bar = 1 μm) and X-ray maps (scale bar = 2 μm) of a region of very fine-grained mesostasis (intimate intergrowth of glass and devitrified mineral grains) in a chondrite from the Semarkona unequilibrated chondritic meteorite. The bright areas in the Ca, Mg and Fe maps are pyroxene and olivine, the brightest areas in the Si and Al maps are the glass from which these crystals formed. Accurate quantitative analyses were able to be performed on each of these phases.

Olivine does not contain any significant amount of Al, so the Al X-ray scan is an indication of the analytical resolution. The 15-85% range for Al at this boundary occurs within a distance of 250 nm, indicating the size of the combined beam diameter and electron excited volume.

With the growing need to study materials at the nm scale, an increasing number of samples of geological interest exist where none of the phases are large enough to be analyzed using a conventional electron microprobe at normal, high voltage conditions.

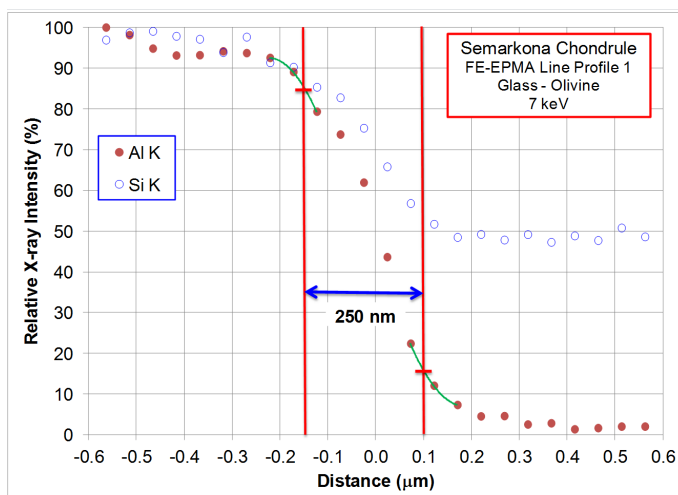
Figure 8 gives an example of such a material, which we were able to fully characterize using a field emission source microprobe operating at 7 keV. The sample is a portion of a high pressure synthesis experiment conducted at Carnegie to mimic conditions thought to occur in the cores of planetary bodies, such as Earth, Mercury and Mars. Mixtures of elements thought to exist in the deep mantles and cores of planetary bodies, in this case Fe metal, MgO , Mg_2SiO_4 , Fe sulfide and Fe oxide, are mixed together and a small portion put between the faces of two diamonds (in a ‘diamond anvil cell’), squeezed up to pressures of 50-100 GPa, and heated

with a laser to temperatures of 1000-2000 K. The material is then cooled and depressurized at controlled rates and the products analyzed (e.g.[6]). Very often in these experiments, the largest phases are just a few μm and most are in the hundreds of nm range.

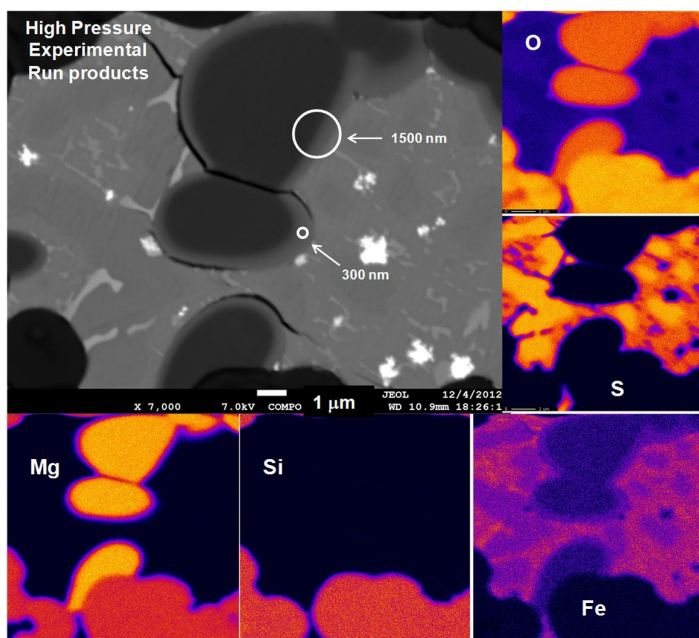
In the experiment result shown in Figure 8, the larger crystals of MgO are surrounded by a Fe metal – S mixture with several different metallic phases with varying S concentrations and possibly sulfides. The grains sizes of the several Fe-S phases are at or less than 1 μm . Partitioning of Fe between the metal, sulfide and oxide phases resulted, in this case, in a zonation of Fe into MgO on the order of 300 nm at the oxide metal boundary. Analyzing at 7 keV, we were able to measure the amount of Fe partitioning without seeing any apparent S concentration due to beam/excited volume overlap at the interface. Using conventional beam energies in a thermionic source microprobe, less than $\sim 20\%$ of the analysis would have come from the area of interest.

CONCLUSIONS

The newly designed field-emission electron microprobe, when operated

**Figure 7**

X-ray line scan at a beam energy of 7 keV across the boundary of glass and an olivine crystal in the mesostasis shown in Figure 6. The distance between the 15% and 85% relative intensity of Al x-rays across this sharp boundary defines the analytical volume of 250 nm. The analytical volume for a conventional thermionic source electron microprobe at 15 keV would encompass more than the entire distance shown in the figure.

**Figure 8**

Backscattered electron image (scale bar = 1 μm) and X-ray maps of the results of heating a mixture of Mg oxide, Mg silicate, Fe metal and Fe sulfide in a diamond anvil cell at high temperature and pressure. Image and maps were collected at a beam energy of 7 keV. A 300-nm wide Fe-rich rim on the central MgO visible in the electron image and Fe X-ray map could be discretely analyzed without seeing any contribution from the surrounding S-rich phases. This would not have been possible using a conventional thermionic source microprobe at 15 keV, where the analytical area would be more on the order of 1500 nm.

a reduced electron beam accelerating voltages (e.g. 7 keV) is capable of X-ray imaging down to 200 nm spatial resolution, quantitative X-ray line scans at a spatial resolution of better than 300 nm and accurate quantitative analyses without contributions from surrounding material for individual grains as small as 300–400 nm. This level of performance provides exciting new capabilities for extending applications of microprobe analyses of geological and materials samples from the micro- to the nano-world.

REFERENCES

1. Erdman, N, Nielsen, C, and Robertson, V.E. Shedding new light on cathodoluminescence – A low voltage perspective. *Microscopy and Microanalysis* vol. 18, pp.1-7, 2012.
2. Castaing R. Electron probe microanalysis. In: *Advances in*

Electronics and Electron Physics, L.L. Marton, and C. Marton, (eds.) Academic Press, 13:317-386, 1960.

3. Drouin, D., Couture, A.R., Joly, D., Tastet, X, Aimez, V., and Gauvin, R. CASINO V2.42: A fast and easy-to-use modeling tool for scanning electron microscopy and microanalysis users; *Scanning* 29:92-101, 2007.
4. Elkins-Tanton, L.T., Draper, D.S., Agee, C.B., Jewell, J., Thorpe, A., Hess, P.C. The last lavas erupted during the main phase of the Siberian flood volcanic province: Results from experimental petrology; *Contrib. Mineral. Petrol.* 153:191-209, 2007.
5. Jones, R. Petrology and mineralogy of type II, FeO-rich chondrules in the Semarkona (LL3.0): Origin by closed-system fractional crystallization with evidence of supercooling, *Geochim.*

- Cosmochim. Acta* 54:1785-1802, 1990.
6. Fei, Y., Wang, Y., and Finger, L.W. Maximum solubility of FeO in (Mg,Fe) SiO₃-perovskite as a function of temperature at 26 GPa: Implication for FeO content in the lower mantle. *J. Geophys. Res.* 101:11525-11530, 1996.

BIOGRAPHY

John Armstrong has a PhD in Chemistry from Arizona State University, (1978). He is now a research scientist and microbeam specialist at the Geophysical Laboratory of the Carnegie Institution of Washington where he directs the SEM and electron microprobe laboratories. He is a past president of the Microbeam Analysis Society. He was formerly the director of analytical facilities in the Division of Geological and Planetary Sciences of the California Institute of Technology, a staff scientist at NIST, and a member of the faculty of the Chemistry Department at the American University, where he still teaches.



ABSTRACT

The electron probe microanalyzer (EPMA) has historically been the premier instrument for microanalysis, but the need to analyze progressively smaller features has driven a revolutionary change in the instrumentation. With an in-lens thermal field-emission gun and an aperture angle control lens, the FE-EPMA is now capable of producing an extremely stable, high-current, electron beam with a diameter nearly an order of magnitude smaller than that possible from a tungsten filament gun, and ideally suited for sub-micrometer analyses.

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