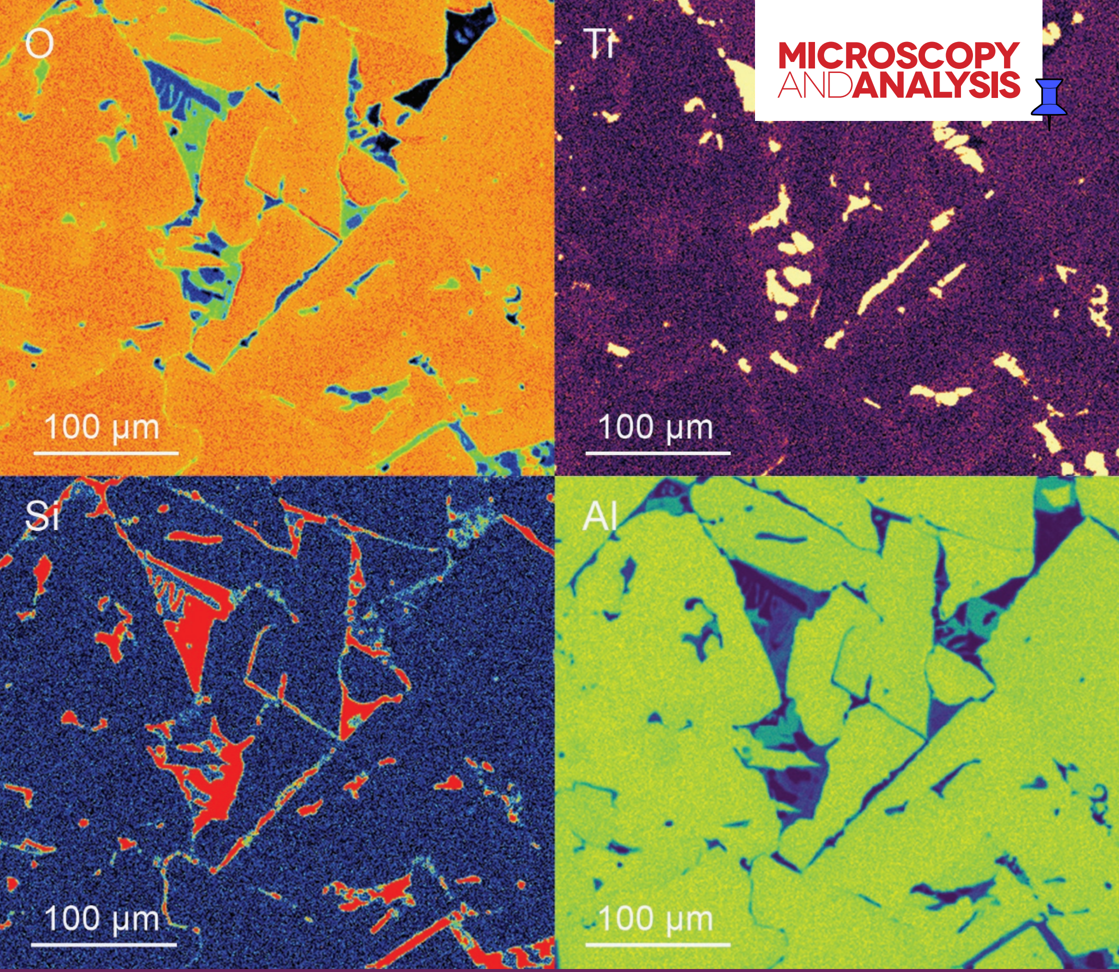

MICROSCOPY AND ANALYSIS

Electron Probe Microanalysis

Essential Knowledge Briefings

Second Edition, 2018

Front cover image: elemental X-ray maps of aggregates of hopper (skeletal) crystals of corundum (Al_2O_3), found in the ejecta from Cretaceous volcanoes on Mount Carmel, Israel. Courtesy of WL Griffin, SEM Gain, T Murphy, O Alard and SY O'Reilly, Macquarie University, Australia.

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About Essential Knowledge Briefings

Essential Knowledge Briefings, published by John Wiley & Sons, comprise a series of short guides to the latest techniques, applications and equipment used in analytical science. Revised and updated annually, EKBs are an essential resource for scientists working in both academia and industry looking to update their understanding of key developments within each specialty. Free to download in a range of electronic formats, the EKB range is available at www.essentialknowledgebriefings.com

INTRODUCTION

Electron probe microanalysis (EPMA) is an analytical technique that has stood the test of time. Not only is EPMA able to trace its origins back to the discovery of X-rays at the end of the nineteenth century, but the first commercial instrument appeared over 60 years ago. Nevertheless, today EPMA remains a widely used technique for determining the elemental composition of solid specimens, with the capability to produce maps showing the spatial distribution of elements over the surface of a sample while also accurately measuring concentration.

EPMA involves bombarding a specimen with a focused electron beam and analyzing the emitted X-rays. Each X-ray is specific to an atom and, after careful energy selection, one may measure the number of atoms in a specific volume, which yields the concentration. The heart of EPMA is a set of wavelength-dispersive spectrometers (WDS) that allow full quantification of the amount of minor and major elements in complex minerals, alloys and materials. Energy-dispersive spectrometers (EDS), which can rapidly collect a full energy spectrum, can also complement the WDS for a quick global check of the composition or major elements.

WDS exhibits far better spectral resolution than EDS, but data collection is not as fast. When combined together in EPMA, EDS and WDS complement each other to produce a powerful analytical instrument.

EPMA has proved particularly adept at analyzing geological materials and metal alloys, able to reveal both the concentration and the distribution of elements at the submicrometer scale. EPMA has also found use in a wide range of other applications, studying everything from the latest advanced solar cells to archaeological material.

This updated Essential Knowledge Briefing provides an introduction to EPMA and its capabilities, as well as the latest instrumentation. It begins with explanations of the operation of the instrument, including details of why elements emit characteristic X-rays, and outlines the major steps in the development of EPMA. It also details various practical issues related to the instrument, describes potential problems that may arise and how to solve them, and provides examples of how EPMA is being used by scientists in their research. Finally, it presents prospective future applications and how the scientists developing these innovative applications help to ensure that EPMA continues to stand the test of time.

HISTORY AND BACKGROUND

EPMA is a multifaceted technique for determining the concentration and the distribution of elements in solid specimens, from major components to trace constituents. The EPMA technique involves bombarding a specimen with an electron beam and then analyzing the emitted X-rays with two different types of spectrometer, a WDS and (optionally) an EDS.

EPMA can identify and analyze all the elements of the periodic table, except for hydrogen and helium, in any solid material. Because the emission of X-rays is largely restricted to the area of the material exposed to the electron beam, EPMA can produce quantitative data on highly localized regions under 1μm in diameter. It has the additional benefit of being non-destructive, meaning that quantitative measurements can be repeated as often as required.

The technique is routinely used to measure elements at trace levels of around 100 parts per million (ppm). With optimized settings, modern EPMA devices can even measure elements at concentrations down to around 10ppm. In addition to spot analyses, EPMA can also map elemental distributions over small or large areas. This is done by either scanning the beam across the surface of the specimen or moving the stage under a fixed beam.

EPMA utilizes an electron beam focused to a very narrow point by magnetic lenses. When this beam hits an atom at the surface of a sample, it can eject electrons from the atom's inner shells (known as K, L and M shells), creating vacancies that are filled by electrons moving down from higher-energy shells. This movement of electrons from outer to inner shells releases energy, which falls into the X-ray range of the electromagnetic spectrum.

The energy of the emitted X-rays corresponds to the energy difference between the shells involved in the transition. As every element has its own unique energy level spacing between shells, this process produces characteristic X-ray emissions that can be used to identify the element.

The origins of EPMA stretch back to the discovery of X-rays in 1895. Although first applied to medical fields, X-rays soon entered the fields of physics and chemistry. At Leeds University, UK, William Bragg and his son Lawrence were famed for their crystallography work using X-rays, which involved developing a critical law relating X-ray diffraction to crystal structure. In 1913, fellow physicist Henry Moseley from the University of Oxford, UK, put Bragg's diffraction law to good use, building a spectrometer to measure the X-ray spectra of elements, based on their diffraction through crystals.

Moseley's X-ray spectrometer used an X-ray tube, potassium ferrocyanide crystals and photographic plates. Moseley was able to bombard samples of available elements, measure the emitted wavelengths and then determine the frequencies of the K and L lines in the spectra (produced by electrons moving from higher-energy shells down to the K and L shells). Importantly, he discovered that plotting the square root of the frequency of the lines against a suitable integer gave straight lines. The integer was revealed to be the atomic number, showing that the elements in any solid sample could be identified by measuring the X-rays emitted. Although Moseley was killed while fighting in World War I, his work had sown the seeds of an analytical revolution.

Meanwhile, developments in electron microscopy were also paving the way for EPMA. In 1932, the German company Siemens built the first electron microscope. In 1944, James Hillier and Richard Baker at RCA Laboratories, Princeton, USA, filed a patent for an 'electronic microanalyzer', which partnered an electron microscope with an energy-loss spectrometer and was able to analyze low atomic number elements. However, they never constructed a working model and post-war communication difficulties meant their development was never widely publicized.

Then, in the late 1940s, Raimond Castaing, a research engineer at the Office National d'Études et de Recherches Aéronautiques (ONERA), a French government research institution for aeronautical applications, developed the first electron microprobe while studying for his PhD. ONERA had obtained two electron microscopes in 1947, and Castaing used the microscopes to investigate the X-rays emitted from alloys bombarded by electrons. Castaing adapted one of the electron microscopes to turn it into an EPMA probe and used a Geiger counter to detect the emitted X-rays, but found that he could not discriminate between elements using this technique. However, he cleverly resolved this issue by building and fitting a spectrometer incorporating a unique quartz crystal to diffract particular wavelengths.

Castaing unveiled this novel technique at the First European Conference on Electron Microscopy in 1950. Castaing's PhD thesis, entitled *Application des sondes électroniques à une méthode d'analyse ponctuelle chimique et crystallographique* (Application of electron probes to a localized chemical and crystallographic analysis method), was published in 1951. This thesis sparked worldwide interest in X-ray microanalysis, and much of the instrumentation and theory set out in it remains valid today.

In the years following Castaing's thesis, ONERA built two prototype electron microprobes, one of which was sent to the Institut de Recherches de la Sidérurgie, a French metallurgy research institute. However, no patent was filed, and industry was quick to see the commercial and analytical potential of the technique. Based on Castaing's prototypes, the French company CAMECA (Compagnie des Applications Mécaniques et Électroniques au Cinéma et à l'Atomistique), a subsidiary of the Compagnie Générale de la Télégraphie sans Fil, was the first to produce a commercial EPMA, the MS85, in 1958 (Figure 1A). CAMECA still develops EPMA instruments today – its latest EPMA generation model, the SXFive, was launched in 2011, and the SXFive-TACTIS (equipped with a touchscreen interface) was announced in December 2017 (Figure 1B).

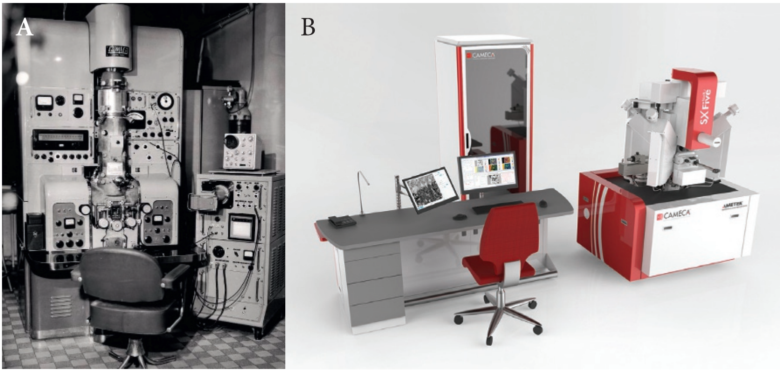


Figure 1. (A) The MS85 – the first model of commercial EPMA. (B) The SXFive-TACTIS, announced in December 2017

Modern EPMA instruments typically possess up to five WDS, each of which is fitted with different diffracting crystals that reflect specific wavelengths. The multiple WDS provide a very precise and accurate analysis, as they have the ability to produce spectra with higher spectral resolution (5–10eV typically) than EDS (120–130eV typically). The latter type of spectrometer can also utilize silicon drift detectors to measure the number of X-ray photons emitted at different energies. This gives a rapid semi-quantitative analysis and is mostly restricted to providing a quick identification of the major elements present in a specimen.

EPMA instruments also house an optical microscope for pinpointing the area of interest and three other types of detectors for capturing the cathodoluminescence (CL), secondary electrons (SEs) and back-scattered electrons (BSEs). These additional signals provide information on the specimen's crystal structure, surface topography, and atomic weight of the surface elements.

Detectors for CL, which is the visible light generated when an electron beam impacts a luminescent sample, provide valuable information not easily generated by other means, especially relating to crystal structure, highlighting trace impurities, lattice defects and crystal distortion. For example, certain CL peaks arise from the energy gap between the conduction band and the valence band in semiconductors, and so can be used to map strain and chemical composition.

For SE imaging, the electron microprobe effectively functions as a scanning electron microscope, providing topographical information based on secondary electrons directly liberated from their energy levels by the electron beam. These electrons have low energies (around 50eV), and only those created within a few nanometers of the sample surface can escape to reach a detector (SEs are therefore very sensitive to surface topography).

Images using BSEs show atomic number differences, based on the fact that the number of BSEs increases with the increasing mean atomic number. In the resulting BSE image, brighter areas indicate heavier mean atomic number (Figure 2). The latest generation of BSE detectors allows enhanced contrast in intensity, especially in the low kV region.

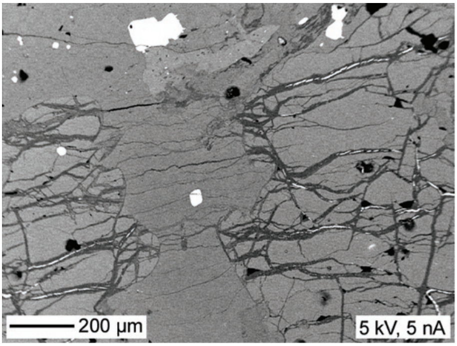


Figure 2. Low kV BSE image of an olivine-rich mineral specimen acquired in 18 seconds

The basic output of EPMA is a spectrum showing peaks that represent X-rays with specific energies or wavelengths, with each peak corresponding to a specific element. The lateral distribution of each element (as shown in Figure 3) is obtained, by either beam or stage scanning, after acquiring intensity at peak and off-peak (background) positions for the different scanned positions. The intensities are then plotted as maps

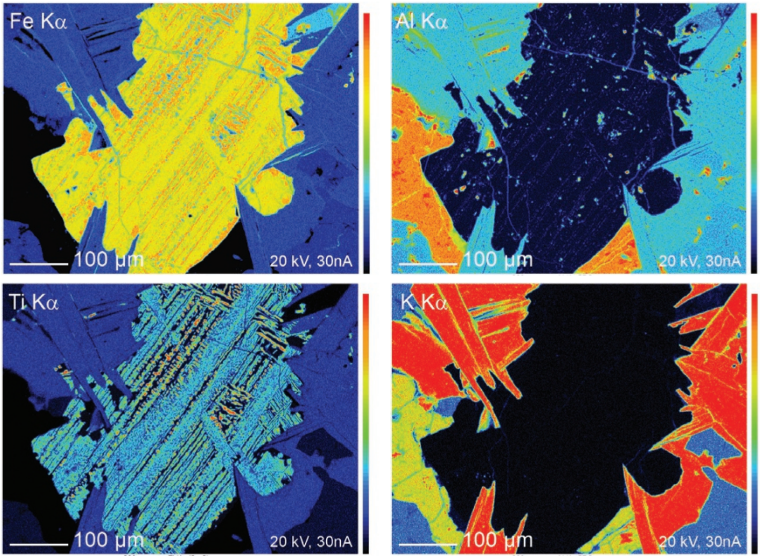


Figure 3. X-ray maps on a nepheline syenite from Ontario, Canada, clearly revealing the elemental distributions

showing the distribution from the measured element across the surface. The sizes and proportions of phases identified in the analyzed material can be determined by combining several X-ray maps.

EPMA can also determine the concentration of elements based on the intensities of the emitted X-rays, allowing it to conduct absolute quantitative analyses. This usually involves first collecting a spectrum with WDS and/or EDS to identify which elements are present in a specimen. Quantitative analysis is then performed using just the multiple WDS detectors, by comparing the X-ray intensities measured for all the elements identified in the initial spectral analysis against standards of known composition. After correction for the effects of fluorescence, absorption and atomic number, the

Point	Na	Mg	Al	Si	K	Ca	Ti	Fe	O	H	Total
1	8.82		10.29	32.14					48.80		100.04
2	3.64	0.60	8.88	19.40	1.53	5.12	1.11	14.64	44.92		99.84
3		5.22	7.16	16.80	8.48		10.11	11.75	40.22	0.42	100.15
4							31.62	36.84	31.62		100.08
5								72.44	27.57		100.01

Table 1. EPMA quantitative compositional data from the nepheline syenite (Figure 3) providing accurate information on fine-scale features. Numbers show the weight percentage at a series of points in the sample

concentrations of all the elements identified in the specimen are accurately determined. The results of quantitative EPMA analyses are commonly displayed as weight percentages of elements and/or oxides (Table 1).

This ability to conduct quantitative analyses is a major strength of WDS EPMA, which is recognized as the only non-destructive analytical technique able to provide absolute and accurate quantification for a specimen of interest. Using well-defined standards, it is possible to achieve quantitative analysis with an accuracy better than ±1%.

IN PRACTICE

The EPMA configuration varies according to the user's requirements, but is always composed of the same main modules: the electron source (gun and alignment column), the microscope, the sample stage, the detectors and some accessories. The electron gun is fitted to a vacuum chamber equipped with a stage that can move the specimen in steps as small as one tenth of a micrometer, allowing the beam to explore the entire specimen surface.

An optical microscope coaxial to the electron beam, and with continuously variable magnification, identifies the exact points of interest on the specimen surface prior to quantitative analysis. A charge-coupled device (CCD) camera allows samples to be viewed in reflected light and thin sections to be imaged in transmitted polarized light. Meanwhile, CL detectors attached to the optical microscope port collect the visible light generated when the electron beam hits the specimen (Figure 4).

Traditionally, the source of the electrons is a heated tungsten filament or a lanthanum hexaboride (LaB_6) cathode, which provides a high-intensity and small-diameter electron beam for high-resolution imaging. However, the implementation of the Schottky emitter field emission gun (FEG) on the EPMA electron column has taken the technique to new analytical heights, improving the lateral resolution and performance at low accelerating voltages.

Analytical lateral resolution is a function of beam diameter and is related to the beam energy, beam current and sample density. Field emission sources produce higher

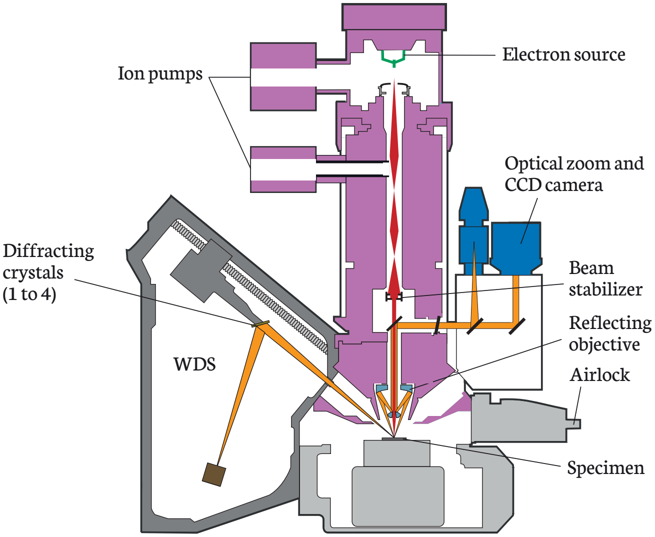


Figure 4. Schematic of EPMA

beam densities at lower energies than conventional LaB_6 and tungsten sources. As a result, they generate narrower beams at higher currents (when using a lower excitation voltage), reducing the region over which scattered electrons generate X-rays (typically known as the 'interaction volume'), to sub-micrometer sizes. Not only does this improve analytical lateral resolution, it also reduces the contribution of secondary fluorescence and decreases charging effects. In scanning electron microscopy mode, a FEG can pick out sample details that are only ~3nm apart, compared with ~6nm for an LaB_6 source and ~7nm for tungsten (Figures 5 and 6).

The EDS collects the entire energy spectrum of the emitted X-rays simultaneously from all elements present in a sample. This qualitative information can be combined with

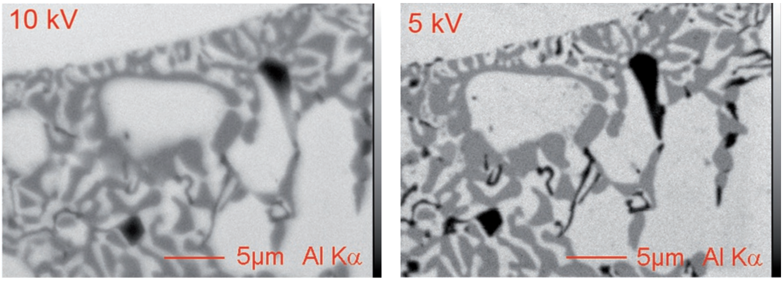


Figure 5. Al Kα X-ray images of a brass specimen at progressively lower voltages (10kV and 5kV) illustrating the improvement of the analytical resolution as a function of impact energy, in agreement with the physics of the experiment

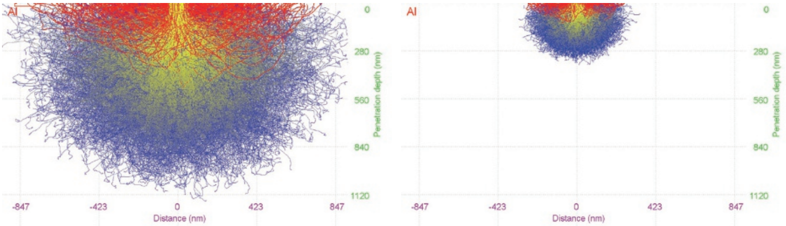


Figure 6. Monte Carlo simulations with the CASINO program (http://www.gel.usherbrooke.ca/casino/) illustrating the decrease of the excitation volume from 10keV to 5keV and the improvement in analytical resolution

information collected by the SE and BSE detectors. The EDS is used to identify the major elements in a specimen but can struggle to identify peaks from minor and trace elements. It produces spectra with quite broad peaks, and peak overlap frequently occurs although this can generally be resolved by deconvoluting the peaks (Figure 7).

What really sets EPMA apart, however, is the series of WDS detectors, each of which measures a single wavelength at a time, making this system the ideal spectrometry tool for quantitative analysis of trace elements. Because the peak-to-background ratio achieved with WDS is much better than for EDS, the minimum detection limits for WDS are at least 10 times lower than for EDS.

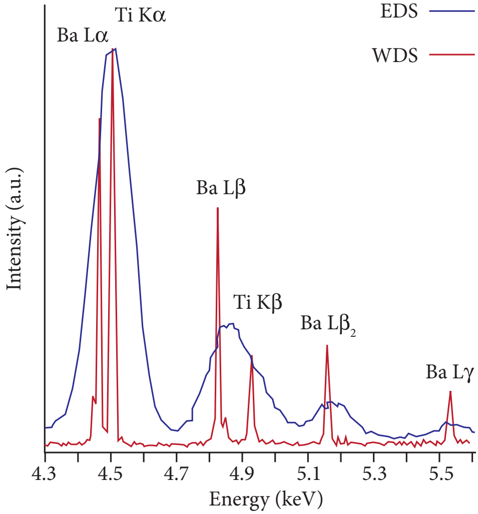


Figure 7. The graph shows X-ray spectra of the same kinetic energy region taken with EDS and with WDS respectively. The order-of-magnitude difference in resolution is obvious, as is the value of higher resolution WDS over EDS in making unambiguous and accurate quantification

Each WDS may contain up to four diffracting crystals dedicated to a given range of X-ray wavelengths. Therefore, the configuration of the WDS is optimized to cover most adequately the application of the user. For example, lithium fluoride (LiF) crystals can detect lines from the K shell for a host of elements, from scandium to rubidium, as well as for L shell lines from tellurium to uranium. Other commonly used crystals include pentaerythritol (PET), thallium acid phthalate (TAP) and synthetic multilayered diffracting crystals (pseudo crystals).

Low-energy (long-wavelength) X-rays require large lattice spacing in the crystals for diffraction. Multilayered crystals are perfect for this purpose, as they maximize scattering efficiency to pick up the wavelengths produced by light elements (beryllium to fluorine).

The measured X-ray intensities, and thus the detection limits, are a function of the number of collected X-rays. Therefore, in order to increase the number of collected X-rays, diffracting crystals with larger surfaces have been developed. All diffracting crystals are now available in larger sizes, allowing faster WDS analysis and improving minimum detection limits thanks to their high counting rates.

As WDS produces spectra with a greater peak-to-background ratio than EDS, it can detect trace elements that are lost in the background noise with EDS. Because of this, EDS is often used to conduct an initial survey of a sample, with WDS subsequently used to check for overlaps, search for trace elements and conduct quantitative analyses. Modern EPMA systems allow simultaneous acquisition of WDS and EDS data, with EDS searching for major elements and WDS targeting the trace constituents.

Raw data produced by the EDS, WDS and other detectors are automatically acquired, processed and analyzed by software supplied with the EPMA, displaying the data as quantitative tables or as X-ray maps. The latest software packages can even combine the two to produce quantitative maps of elemental distribution, increasing the throughput efficiency (Figure 8).

This level of analytical capabilities allows researchers to use EPMA to study a wide variety of different materials, with particular emphasis on geological materials and metal alloys. EPMA can identify small intermediate phases, typically a few

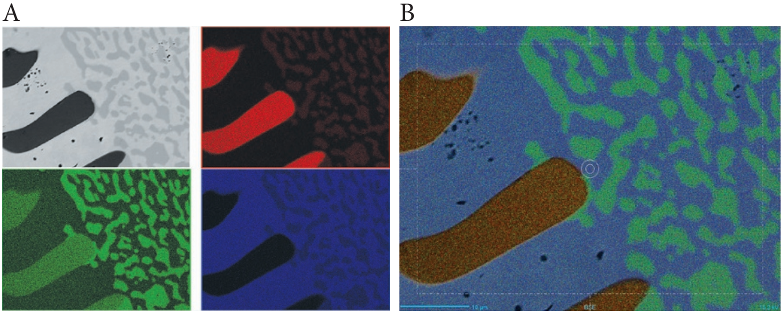


Figure 8. The latest CAMECA EPMA model allows the acquisition of real-time WDS and EDS X-ray images in one click, either in composite (A) or superposed mode (B), producing a rapid yet meaningful overview of the specimen composition

hundreds of nanometers in size, in geological materials such as metal ores, volcanic rocks and meteorites. It can also be used to date geological samples containing monazite, which is found in many types of rock, as a complement to isotopic ratio measurements. Known as geochronology, this technique measures concentrations of uranium, thorium and lead, and allows calculation of the age of the sample based on the fact that lead would not have been present at the time of monazite crystallization.

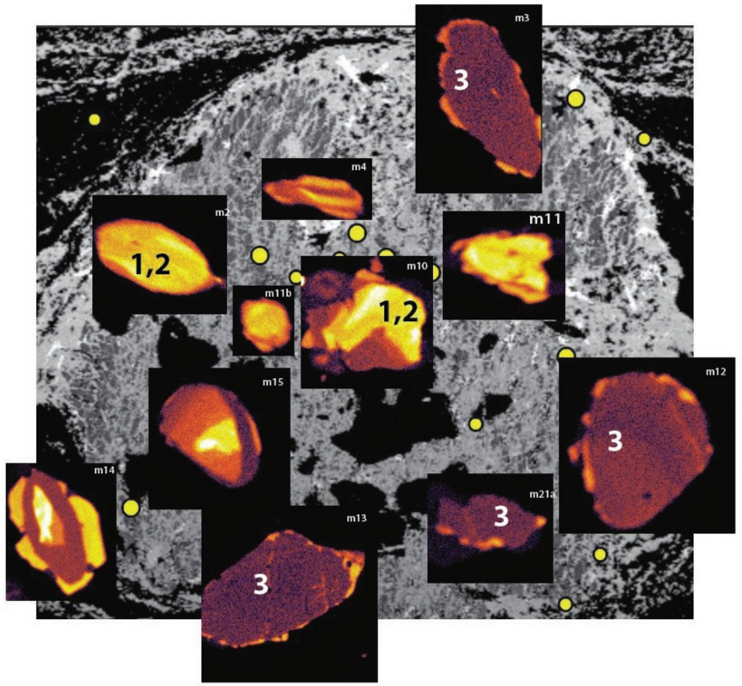
EPMA is regularly used to investigate the chemical structure of newly developed metal alloys and how such structure is altered in response to activities such as thermal processing and corrosion. But researchers also use it to study various other synthetic materials, such as glass and ceramics, as well as archaeological material like ancient pots and bronze artefacts. It has even been used to study various types of natural material, including bone and soil.

CASE STUDY 1. From single-grain geochronology to multiscale petrochronology

Since 1998 the EPMA laboratory at the University of Massachusetts, USA, has been developing and refining techniques for geochronological analysis, particularly of monazite, using their SX50 and SX100 'UltraChron' instruments – the latter, a unique instrument optimized for quantification of U, Th and Pb and developed in collaboration with CAMECA and with the support of the US National Science Foundation. The primary intent was, and continues to be, to obtain the most accurate geological age determinations possible by non-destructive in situ *analysis of the geochronometers monazite and xenotime (REE-Y-phosphates). These minerals crystallize with substituent Th and U but negligible Pb, and on geological timescales the decay of their Th and U produces ingrown Pb. Therefore a sufficiently precise and accurate EPMA analysis of parent Th and U, and daughter Pb, allows accurate age determinations of extremely small domains – often only a few micrometers wide – within these geochronometer minerals.*

In metamorphic rocks with long and complex deformational and thermal histories, these events are recorded in monazite crystals typically only tens of micrometers in size. Up to five distinct compositional and age domains have been documented within a single small crystal,[1] *and such complexity can only be unraveled and understood by initial WDS mapping of characteristic trace elements in the crystal to identify subdomains for quantitative analysis by EPMA or other techniques.*

As methods were refined at the University of Massachusetts, it soon became apparent that WDS 'multiscale mapping' could extend single-point and single-crystal EPMA age measurements into the emerging realm of petrochronology – which places geochronometer minerals and their age domains into the overall context of the deformational fabrics in the specimen, and the compositional subdomains in which the geochronometers participate in chemical reactions with their silicate host minerals.[2] In



Multiscale mapping: 2.6Ga (billion-year-old) gneiss specimen from northern Canada, with complex thermal and deformational history to 1.8Ga. Compositional subdomains in monazite record these events. WDS grain maps (Y) are shown with grain locations (yellow dots) indicated on a large-area base map (Mg). The cm-scale Mg-rich phase in the base map is garnet

multiscale mapping, the entire approximately 2x4cm specimen is first mapped at coarse scale for elements such as Mg, Ca, K to determine the disposition and zonation in the silicate matrix minerals. Ce, Y and/or Zr are also mapped to locate all the monazite, xenotime and/or zircon crystals in the specimen. Every geochronometer mineral in the specimen can then be evaluated in context and a subset selected for further analysis.

Each target grain is then mapped at high resolution for characteristic minor elements (typically Y, Th, U, Ca, Si for monazite) to identify compositional and thus chronological subdomains. The grain maps are then placed within the larger whole-specimen WDS maps. Crucially, all the WDS minor element grain maps with their raw pixel intensities are processed simultaneously, allowing the correlation of the various compositional subdomains across the whole specimen. Most grains contain only a subset of all the information in the entire specimen, and the correlation of these subdomains across the specimen by WDS multiscale mapping enables not only more conventional geochronology but also comprehensive petrochronology.

1. Mahan KH, Goncalves P, Williams ML, Jercinovic MJ. Dating metamorphic reactions and fluid flow: application to exhumation of high-*P* granulites in a crustal-scale shear zone, western Canadian Shield. *J Metamorph Geol* 2006;24:193–217. (https://doi.org/10.1111/j.1525-1314.2006.00633.x)
2. Williams ML, Jercinovic MJ, Mahan KH, Dumond G. Electron microprobe petrochronology. *Rev Mineral Geochem* 2017;83:153–82. (https://doi.org/10.2138/rmg.2017.83.5)

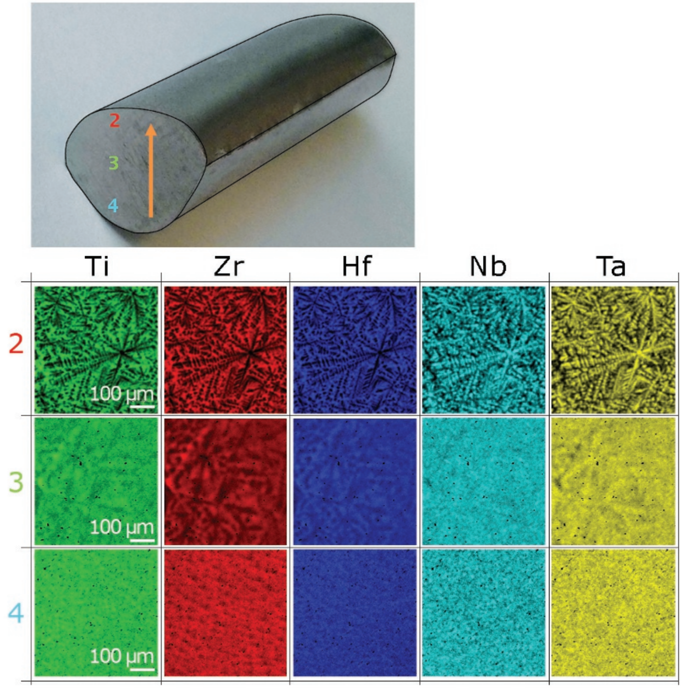
CASE STUDY 2. Quantitative analysis of microstructure in novel metallic alloys

Metal alloys are the main focus of the EPMA studies conducted by Dr Eric Leroy at the Institute of Chemistry and Materials Paris-Est in France. 'In my laboratory, we synthesize different types of metallic alloys: rare earth, aluminium or different types of intermetallics,' he explains. 'The main purpose of my analyses is to obtain the microstructure of the samples and the compositions of the phases.'

New metallic alloys are becoming increasingly complex, made up of many different metallic elements at similar concentrations rather than just one or two major constituents and a few minor ones for the optimization of final properties.

Leroy and his team recently developed a refractory high-entropy alloy (HEA) with near-equimolar TiZrHf-NbTa composition by combined arc melting and induction techniques.[1,2] *This new alloy shows promise for applications as a structural material, especially at high temperatures. Analysis with the CAMECA electron microprobe operating at 15kV provided precise and accurate X-ray maps and quantitative data revealing the diversity of microstructural features in various ingot zones at different cooling rates.*

A dendritic microstructure is observed in the alloy zone 2 that has been slowly cooled directly at the contact of the argon atmosphere of the arc-melting. This dendritic structure tends to disappear in the central and in the lower parts of the ingot (zones 3 and 4), where the alloy is directly in contact with water-cooled copper plate, ie *corresponding to a higher solidification rate.*



General view of the as-cast ingot and EPMA element map

Ingot zone	Ti	Zr	Hf	Nb	Ta
2	20.59	19.45	20.14	18.41	21.4
3	21.09	20.41	20.54	17.63	20.33
4	20.86	20.07	20.42	17.76	20.89
Global	20.85	19.98	20.37	17.93	20.87

Quantification of the chemical composition (at.% average) for the different ingot zones selected in the figure above

'The major information obtained by EPMA is the accurate chemical composition and the X-ray maps,' says Leroy. 'Sometimes I also use EPMA for the characterization of multilayered

samples; in this case, the information wanted is thickness and the composition of the layers.'

But Leroy hasn't entirely restricted his use of EPMA to metallic alloys. For example, he has used it to determine the chemical composition and microstructure of grains in a sediment core taken from a swamp in the Pacific islands of Vanuatu.[3] *This helped to reveal how the environmental conditions on the islands have changed over the past 6500 years.*

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3. Wirrmann D, Eagar SH, Harper MA, *et al*. First insights into mid-Holocene environmental change in central Vanuatu inferred from a terrestrial record from Emaotfer Swamp, Efaté Island. *Quat Sci Rev* 2011;30:3908–24. (https://doi.org/10.1016/j.quascirev.2011.10.003)

PROBLEMS AND SOLUTIONS

As with any analytical technique, EPMA does have some limitations and restrictions. It cannot identify hydrogen or helium in specimens, due to the fact that hydrogen and helium atoms only possess electrons at one energy level. This means EPMA is not optimal for analyzing hydrous minerals.

Also, like other analytical techniques, to get the most out of EPMA, users need to optimize operating conditions for their own particular specimen, instrument configuration and analytical requirements. For example, the specimen needs to be clean, flat and finely polished. Surface imperfections can interfere with electron–sample interactions and make experimental set-up trickier, requiring carefully selected angles for the spectrometers. When mounted in a vertical position, orthogonal to the surface of the specimen, WDS is highly sensitive to sample roughness and positioning. Sample roughness and incorrect positioning can lead to a loss of up to 70% of the emitted X-rays. This can be resolved by tilting the WDS, as an inclined WDS is far less sensitive to the X-ray source position, and then using the optical microscope to align the WDS on the specimen. Using a tilted spectrometer allows samples with a roughness of a few millimeters to be measured.

Electrically insulating specimens need to be coated with a thin film of a conducting material such as carbon to minimize the charging effects and to reduce specimen heating. Failure to coat samples will lead to them becoming electrically charged, making them impossible to analyze. Once the specimen has been loaded onto the stage, the sample chamber is pumped to high vacuum (10^{-5}–10^{-6}Pa) to prevent gas and vapor molecules from interfering with the electron beam. The accelerating voltage and electron beam current then need to be carefully selected and the electron beam optimally focused.

Critical electron beam parameters

Accelerating voltage and beam diameter are the two most important parameters to optimize for quantitative X-ray analysis. Optimum conditions are obtained when the analytical spatial resolution is primarily limited to the diameter of the X-ray emission volume in a specific material.

Field emission guns can produce extremely small diameter and bright beams especially at low beam voltages (100nm @ 10keV and 10nA). This is a great advantage for high lateral resolution analyses, as low beam voltages reduce the diameter of the X-ray emission volume. However, low beam voltages can only excite low-energy X-rays (K lines for elements with an atomic number below 22, and L and M lines for elements with higher atomic numbers). For quantification, the use of low-energy X-rays is also challenging as they are subject to larger peak shifts, more peak interferences and lower fluorescence yields compared to higher energy K lines. Peak interferences can be resolved using specific software, and accurate quantification with low-energy X-rays can be achieved by using Ll lines (Figures 9 and 10).

Challenges specific to quantitative analysis

The parameters that are important to optimize when conducting trace analysis include beam conditions, spectral

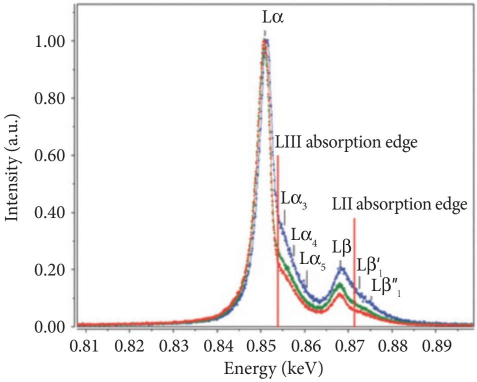


Figure 9. Ni Lα Lβ spectral range in pure nickel acquired at 5keV (blue), 10keV (green) and 15keV (red) revealing modification in shape and peak positions

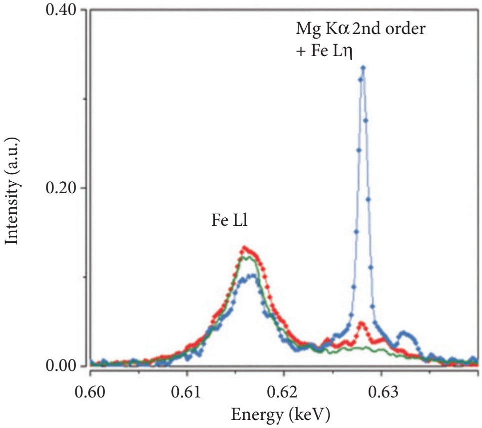


Figure 10. Fe Ll spectral range in pure iron (green), haematite (red), and almandine (blue) showing accurate quantification of the first series transition metals

conditions (energy resolution, background positions, interferences) and analysis time. Trace analysis at the highest levels of sensitivity requires both high beam energies and high beam currents (in the range of 100nA to 200nA) to produce as many X-ray counts as possible for the element of interest. These parameters are easily accessible through dedicated EPMA software.

For any quantitative analyses, the quality of the data depends on beam current stability and on the reproducibility, sensitivity and spectral resolution of the WDS.

Both trace and quantitative analyses with EPMA are reliant on the multiple WDS detectors to provide data with greater spectral resolution and a greater peak-to-background ratio than EDS. Nevertheless, WDS peaks still need to be separated from a background of continuum radiation resulting from inelastic collisions by incident electrons in the specimen. The solution involves calculating background intensities at spectral peak positions by interpolating between count rate measurements collected on both sides of the peaks.

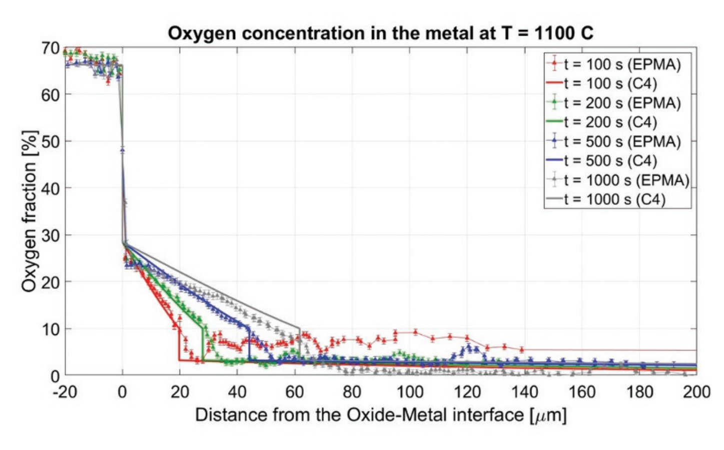
CASE STUDY 3. Optimization of nuclear structural materials

Being able to predict zirconium alloy corrosion kinetics during a loss-of-coolant accident (LOCA) high-temperature transient is critical to assess the mechanical integrity of nuclear fuel cladding.[1,2] *Researchers from the Department of Engineering Physics at the University of Wisconsin-Madison, USA, have developed a physically based corrosion model called the Coupled-Current Charge Compensation (C4) model.*[3,4] *They are using the SXFive field emission electron probe microanalyzer located in the Geoscience Department to validate the model with accurate experimental oxygen concentration profiles in Zircaloy-4 sheet samples.*

Experimental studies on high-temperature corrosion of zirconium alloys usually yield oxygen weight gain, oxide thickness and α-Zr layer thickness.[5] *However, none of these can yield the actual oxygen concentration profile in the fuel cladding, even though it is a crucial parameter to assess its mechanical strength. Hence, the new study performed at the University of Wisconsin-Madison focused on obtaining oxygen concentration profiles using EPMA at 15kV with 20nA of Faraday current with a fully focused beam.*

The graph opposite compares several experimental oxygen concentration profiles obtained at different oxidation times as a function of depth in the cladding to the prediction of the C4 model. From the sample surface to the bulk, we observe sequentially: (1) The oxide layer with a constant oxygen concentration of 66.7at.%; (2) the oxygen-stabilized α-Zr layer showing a linear variation of *oxygen concentration from 28at.% to 10at.%; (3) the prior-β-Zr layer with an oxygen concentration varying below 5at.%.*

Overall, the experimental data obtained with EPMA successfully validate the C4 model prediction. Only the use of WDS on the EPMA enables the experimental validation of oxygen concentration profile predictions, because EDS does not have enough sensitivity to resolve the concentration drop from 10at.% to 5at.% at the interface between the α-Zr and the prior-β-Zr phase.



Oxygen concentration profiles in Zircaloy-4 sheet coupons oxidized at 1100°C for 100 to 1000 seconds. Courtesy of Léo Borrel and Adrien Couet, University of Wisconsin-Madison

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WHAT'S NEXT?

As highlighted in the *History and Background* section, EPMA is not a new analytical technique, with the first commercial system introduced in 1958. Although the underlying technology has improved greatly since then, the basic principles of EPMA are exactly the same. So why does EPMA remain such a popular and commonly used analytical technique after more than half a century?

The main reason is that it is still the only non-destructive analytical technique that can accurately determine the concentration of almost any element in almost any solid material, whether crystalline or amorphous. This inherent ability has recently been enhanced by the improved resolution offered by new electron beam sources and the ease of use provided by the latest software tools. Nevertheless, there is still a certain amount of room for improvement.

EPMA can struggle with the analysis of light elements such as carbon and oxygen, as these elements generate low-energy X-rays that can be difficult to distinguish from background noise. Recent technological advances have improved the situation, though, with modern, high-resolution EPMA instruments, utilizing a FEG and multiple WDS, now able to identify and quantify all the light elements down to beryllium.

Developers of EPMA instruments are also experimenting with using new multilayer crystals in WDS to improve the detection of lighter elements. In many cases, synthetic crystals, also known as pseudo crystals, are better than conventional ones, giving higher count rates and helping to dampen unwanted higher-order reflections. Developers are also working to reduce the time it takes to collect WDS spectra by, for example, using multichannel analyzers.

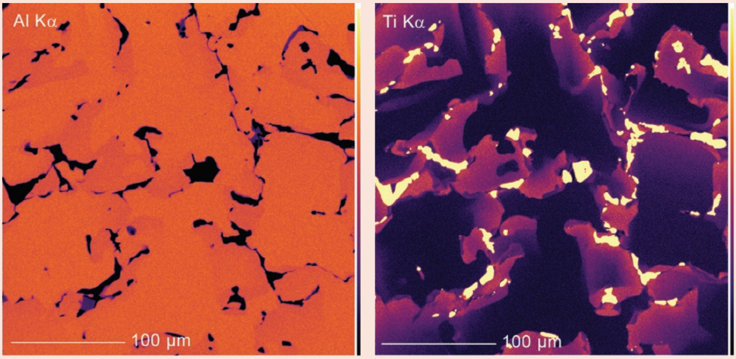
The range of materials that EPMA is being used to examine is also expanding all the time, as new materials are continually developed. For example, over the past few years scientists have used EPMA to study the distribution of silver nanoparticles on titanium oxide nanotubes and the composition of solar cells made from thin films of copper, tin and sulfur.

CASE STUDY 4. EPMA analysis of fluid inclusions in volcanic rocks

Professor William L Griffin and his teams at the Macquarie University Department of Earth and Planetary Sciences, Australia, have used EPMA in a wide range of petrological and geochemical research projects, focusing among others on the composition and evolution of the crust–mantle system, fluid and melt-related processes in the Earth's mantle, as well as in-situ *microanalysis of trace elements in ore deposits to support the mining industry.*

Investigating unusual mineral assemblages found in volcanic rocks from Tibet or Kamchatka, they reveal that interactions between magma and methane-hydrogen fluids derived from the deep Earth may generate highly reducing conditions within some volcanic plumbing systems. More recently, they gained further insights into these unrecognized fluid transfer processes via the super-reduced mineral system observed in Cretaceous volcanic rocks from Mount Carmel, Israel. This mineral system appears to reflect the local interaction of mantle-derived $CH4^{+}/^{-}H2$ *fluids with basaltic magmas in the shallow lithosphere. These interactions produced desilication of the magma, supersaturation in* Al_2O_3*, leading to rapid growth of corundum.*[1–3]

The sample shown overleaf is a corundum (Al_2O_3*) found in Mount Carmel volcanic ejecta analyzed with the Macquarie SX EPMA. The crystal morphology indicates rapid growth from a high-T melt supersaturated in aluminium oxide. The growth of the crystals has trapped pockets of the melt, which now consist of glass and a range of Ti-rich phases. The increase in Ti and* *decrease in Al toward the melt pockets reflects the substitution of Ti for Al, up to 2.5 wt% Ti. These EPMA elemental distributions correlate well with Professor Griffin's previous published data, measurements showing that the Ti is present as Ti*$^{3+}$*, rather than in the normal Ti*$^{4+}$ *valence.*



Titanium and aluminium distribution in corundum measured at 15kV

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Conclusion

With its unique ability to identify and quantify elements in solid samples with great sensitivity and high accuracy, EPMA has been at the forefront of analytical technology for over 60 years. As the analytical demands of scientists have increased and the range of materials they want to study has grown, EPMA has managed to stay relevant. This is partly because of the inherent advantages of the technology, which were apparent from the very beginning, and partly because of the advances that have occurred over the past 60+ years, such as high-resolution electron beams and sophisticated software. With no sign that the ability to identify and quantify elements in solid samples will become any less useful or valuable in the future, EPMA's position is probably secure for at least the next 50 years as well.

FURTHER INFORMATION

CAMECA website. (http://www.cameca.com/products/epma/sxfive)

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