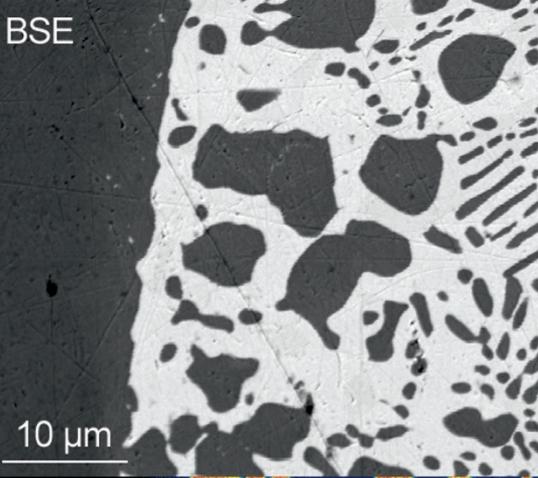
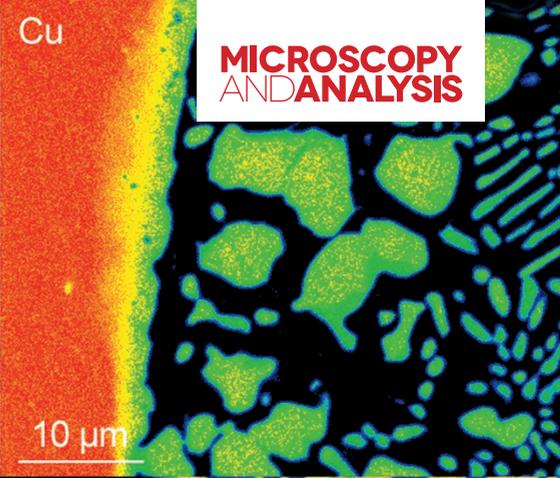


BSE

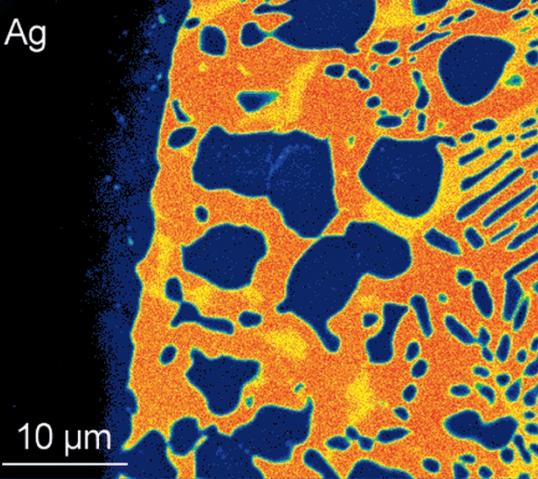


Cu

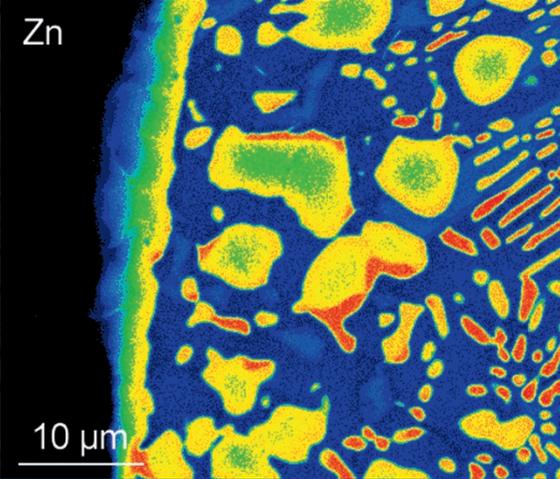


**MICROSCOPY
AND ANALYSIS**

Ag



Zn



Electron probe microanalysis



Essential
Knowledge
Briefings

First Edition, 2015

 **CAMECA**[®]
SCIENCE & METROLOGY SOLUTIONS

 **AMETEK**[®]
MATERIALS ANALYSIS DIVISION

Front cover image: high-resolution X-ray maps of copper (Cu), zinc (Zn) and silver (Ag) illustrating the interdiffusion zone between the main material (Cu) and the brazing material (Ag-Zn). Data acquired with the SXFiveFE at 10keV, 30nA

© 2015 John Wiley & Sons Ltd, The Atrium, Southern Gate,
Chichester, West Sussex PO19 8SQ, UK
Microscopy EKB Series Editor: Dr Julian Heath
Spectroscopy and Separations EKB Series Editor: Nick Taylor

CONTENTS

4 INTRODUCTION

6 HISTORY AND BACKGROUND

13 IN PRACTICE

22 PROBLEMS AND SOLUTIONS

28 WHAT'S NEXT?

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 50 years ago. Nevertheless, EPMA remains a widely used technique for determining the elemental composition of solid specimens, able to produce maps showing the distribution of elements over the surface of a specimen while also accurately measuring their concentrations.

EPMA involves bombarding a specimen with a focused electron beam and analyzing the emitted X-rays. It generally combines two related analytical techniques - wavelength-dispersive spectroscopy and energy-dispersive spectroscopy (which is also the subject of a separate Essential Knowledge Briefing) - in a single instrument known as a microprobe. Both techniques work by collecting characteristic X-rays and continuum released when the surface of a specimen is bombarded with electrons. As their names suggest, wavelength-dispersive spectroscopy separates emitted X-rays according to their wavelengths while energy-dispersive spectroscopy separates them according to their energies.

Wavelength-dispersive spectroscopy exhibits far better spectral resolution than energy-dispersive spectroscopy, but data collection is not as fast. When combined together in EPMA, energy-dispersive spectroscopy and wavelength-dispersive spectroscopy complement each other to produce a powerful analytical instrument. Energy-dispersive spectroscopy can conduct a quick initial analysis to identify the major elements, while wavelength-dispersive spectroscopy can perform a more detailed analysis to identify trace elements and measure the concentrations accurately.

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 sub-micrometer 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 Essential Knowledge Briefing provides an introduction to EPMA and its capabilities. It begins with a detailed explanation of the operation of the instrument, including an explanation of why elements emit characteristic X-rays, and outlines the major steps in the development of EPMA over more than 100 years. 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 looks at prospective future applications and how the scientists developing these innovative applications will help to ensure that EPMA continues to stand the test of time.

HISTORY AND BACKGROUND

EPMA is a multi-faceted technique for determining the concentration and the distribution of elements in solid specimens, from major elements 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 wavelength-dispersive spectrometer (WDS) and an energy-dispersive spectrometer (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 spots under 1 μ m 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 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 that holds the specimen in relation to 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 high-energy shells (known as K, L and M shells), creating vacancies that are filled by electrons moving from the atom's outer low-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 lower 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 a 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 cristallographique* (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 remain 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. CAMECA still develops EPMA instruments today - its latest model the SXFive was launched in 2011 (Figure 1).

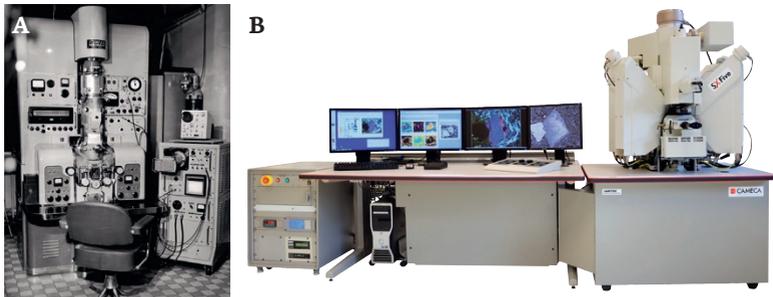


Figure 1. (A) The MS85 - the first model of commercial EPMA. (B) The SXFive - CAMECA's latest EPMA generation

As quantum entities, X-rays have characteristics of both particles and waves and so can be detected by either their energies or their wavelengths, which is why EPMA instruments utilize both EDS and WDS. For the EDS, EPMA instruments 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.

In contrast to a single EDS, modern EPMA instruments typically possess up to five WDSs, each of which is fitted with different

diffracting crystals that reflect specific wavelengths. The multiple WDSs provide a more precise and accurate analysis, as they have the ability to produce spectra with higher spectral resolution (5–10eV typically) than EDS (120–130eV typically).

EPMA instruments also house an optical microscope for pinpointing the area of interest and three detectors for capturing the cathodoluminescence (CL), secondary electrons (SE) and back-scattered electrons (BSE) that are also emitted from the specimen under electron bombardment. These additional signals provide information on the specimen's crystal structure, surface topography and atomic weight.

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 and only those created within a few nanometers of the sample surface can escape; secondary electrons 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.

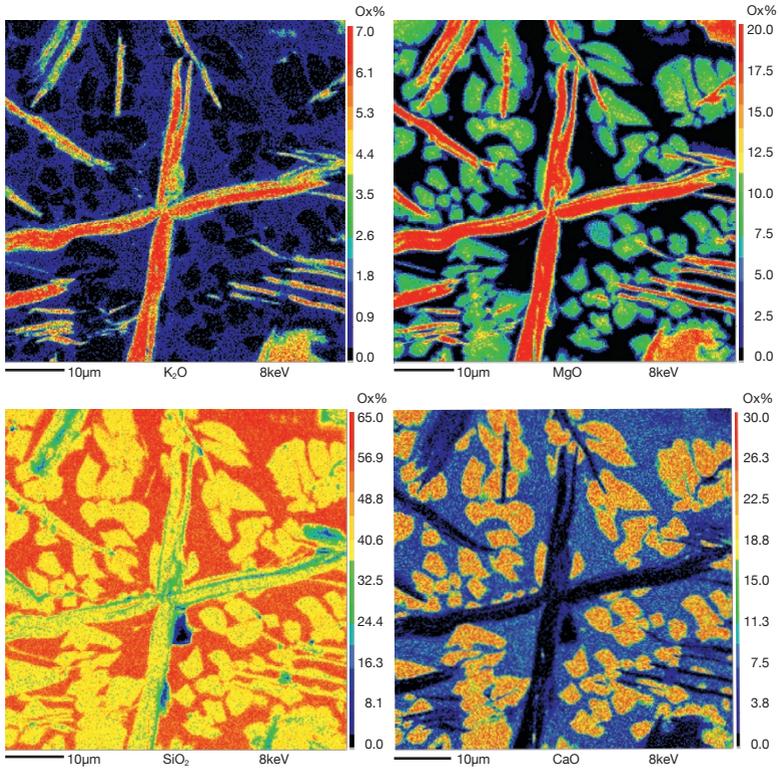


Figure 2. X-ray maps acquired at high magnification on synthetic volcanic rock clearly reveal three phases: clinopyroxene (no K_2O), glass (with 2% of K_2O) and phlogopite (with 5% of K_2O). Data courtesy of Ida di Carlo, Institut des Sciences de la Terre d'Orléans, France

The basic output of EPMA is a spectrum showing peaks that represent X-rays with specific energies (EDS) or wavelengths (WDS), with each peak corresponding to a specific element. The lateral distribution of each element is obtained, by either beam or stage scanning, after acquiring X-ray maps at peak and off-peak (background) positions. The sizes and proportions of phases identified in the analyzed material can be determined by combining several X-ray maps (Figure 2).

Point	Na ₂ O	K ₂ O	MgO	CaO	FeO	Al ₂ O ₃	SiO ₂	TiO ₂	H ₂ O	O=F	Total
1	0.430	5.097	16.324	0.124	11.885	14.285	46.081	1.364	4.287	0.006	99.871
2	0.486	5.338	16.068	0.257	12.606	14.228	45.572	1.344	4.269	0.010	100.158
3	0.581	6.918	18.908	0.283	12.647	13.681	41.821	1.107	4.182	0.003	100.125
4	0.472	5.024	16.154	0.223	12.142	13.561	45.935	1.415	4.242	0.014	99.155
5	0.492	4.836	16.924	0.522	12.622	13.253	46.717	1.181	4.305	0.016	100.836
6	0.663	5.851	17.593	0.417	12.949	13.431	43.994	1.190	4.236	0.000	100.324
7	0.466	5.640	15.805	0.461	12.957	14.095	44.938	1.217	4.241	0.006	99.815
8	0.623	4.949	17.091	0.328	12.949	14.001	44.621	1.059	4.252	0.000	99.873

Numbers show the oxide weight percentage at a series of points in the sample.

Table 1. Quantitative compositional data for a synthetic volcanic rock at high temperature and high pressure. Data courtesy of Ida Di Carlo, Institut des Sciences de la Terre d'Orléans, France

EPMA can also determine the concentration of the 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 WDSs, by comparing the X-ray intensities measured for all the elements identified in the initial spectral analysis against standards of known composition. After matrix correction for fluorescence, absorption and atomic number effect, the 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 $\pm 1\%$.

IN PRACTICE

The EPMA configuration varies according to the user's requirements, but is always centered on an electron gun that fires beams of electrons at the specimen. 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. 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 3).

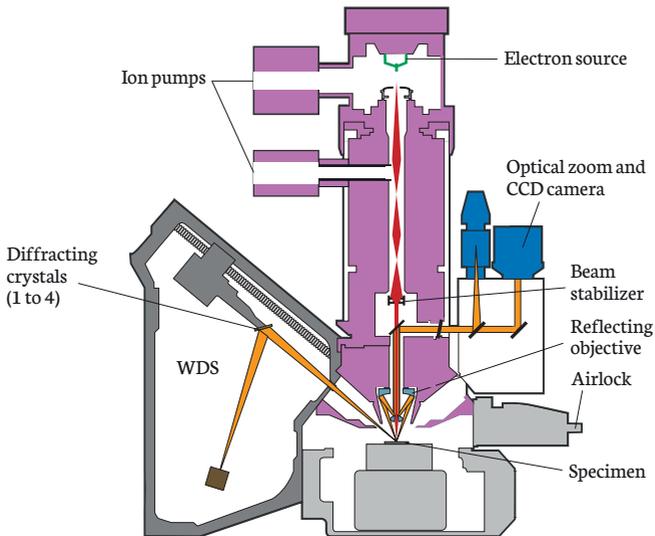


Figure 3. Schematic of EPMA

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 beam densities at lower energies than conventional LaB_6 and tungsten sources. As a result, they generate narrower beams at higher currents, reducing the region over which scattered electrons generate X-rays, 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 $\sim 3\text{nm}$ apart, compared with $\sim 6\text{nm}$ for an LaB_6 source and $\sim 7\text{nm}$ for tungsten.

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 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 4).

What really sets EPMA apart, though, is the series of WDSs, each of which measures a single wavelength at a time, making this

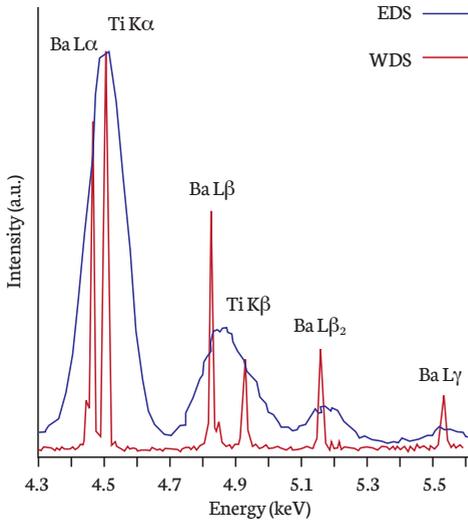


Figure 4. The graph shows X-ray spectra of the same kinetic energy region taken with EDS and with WDS respectively. The order-of-magnitude difference in resolution is obvious, as is the value of higher resolution WDS over EDS in making unambiguous and accurate quantification

system the ideal spectrometry tool for quantitative analysis of trace elements. Because the peak-to-background ratio achieved with the WDS is much better than for EDS, the minimum detection limits for WDS are at least 10 times lower than for EDS.

Each WDS may contain up to four diffracting crystals dedicated to a given range of X-ray wavelengths, with each WDS using different crystals to cover the entire X-ray spectrum. 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 multi-layered diffracting crystals (pseudo crystals).

Low-energy (long-wavelength) X-rays require large lattice spacing in the crystals for diffraction. Multi-layered crystals are perfect for this purpose, as they maximize scattering efficiency to pick up the wavelengths produced by the 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, hunt for trace elements and conduct quantitative analyses. Alternatively, some 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 instrument's throughput efficiency.

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 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 is 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 this 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 different types of natural material, including bone and soil.

CASE STUDY 1

When the Icelandic volcano Eyjafjallajökull erupted in 2010, teams from the University of Iceland and the University of Edinburgh, UK, were among the first to reach the scene. These teams were keen to analyze the rapidly descending layers of volcanic ash, or tephra, in order to understand the eruption, including its adverse effects on air transport.^{1,2}

Important within this research was the study of melt inclusions – tiny pockets of magma, as small as 10µm across or less, trapped within crystals that grow while the magma rises from its sources deep in the Earth’s crust towards the volcanoes. The ascending magma progressively releases volatile elements such as fluorine, chlorine and sulfur, forming atmospherically damaging gases including hydrogen fluoride and sulfur dioxide. Comparing volatile concentrations in the earliest trapped inclusions – reflecting the original magma composition – and the glass formed when the magma freezes upon eruption – its final volatile content – allows estimates to be made of the amount of gasses released. This can give an indication of the environmental impacts of the eruptions.

Studying tephra involves using EPMA in ‘quite an unusual way’, with extremely low beam currents, says Dr Chris Hayward at the University of Edinburgh. This is because these glassy materials can suffer chemical changes (principally loss of sodium) during analysis, especially of small areas.

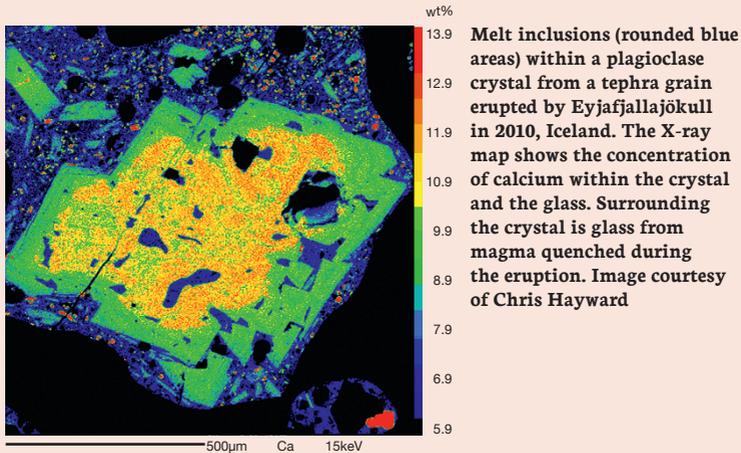
Hayward and his team have developed new EPMA methods that allow them to carry out high-quality analyses of tephra layers that were previously impossible. These high-resolution methods rely on Edinburgh’s CAMECA instrument, which permits stable beam

currents down to 0.5nA and allows three separate beam currents during a single analysis. Both these features are essential for conducting measurements at the small beam size ($3\mu\text{m}$) required to ensure that sodium and potassium are kept within the analysis volume.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
Av (wt%)	62.06	0.25	18.11	4.49	0.14	0.12	1.07	8.34	5.41	0.03	100.04
1 σ St Dev	0.81	0.01	0.62	0.30	0.02	0.03	0.09	0.72	0.22	0.01	
Det Lim (ppm)		100			238	261	532		88		

Av, average; St Dev, standard deviation; Det Lim, detection limits.

Quantitative EPMA data for Mount Edziza sheep-track tephra with $3\mu\text{m}$ beam diameter (average of 27 points)



1. Hayward C. High spatial resolution electron probe microanalysis of tephras and melt inclusions without beam-induced chemical modification. *Holocene* 2012;22:119-25. (<http://dx.doi.org/10.1177/0959683611409777>)
2. Gudmundsson MT, Thoordarson T, Hoskuldsson A, *et al.* Ash generation and distribution from the April-May 2010 eruption of Eyjafjallajökull, Iceland. *Sci Rep* 2012;2:572. (<http://dx.doi.org/10.1038/srep00572>)

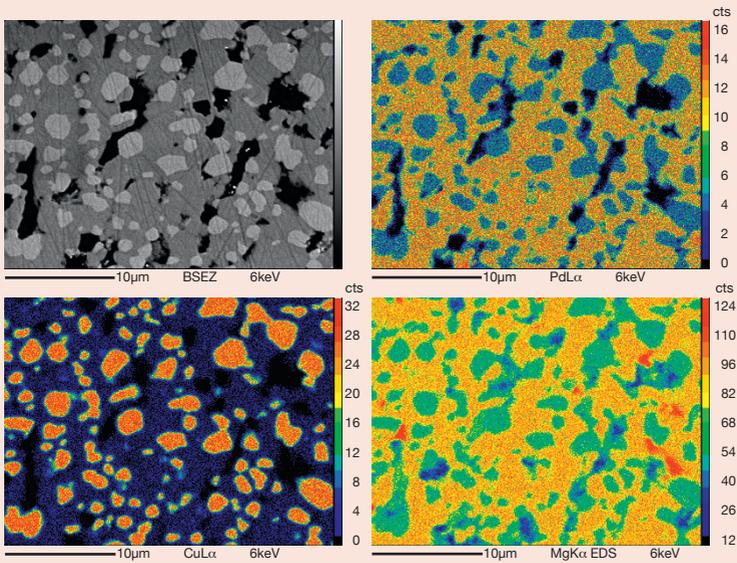
CASE STUDY 2

Metal alloys are the main focus of the EPMA studies conducted by Dr Eric Leroy at the Institute of Chemistry and Materials Paris-East 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.’

These new metallic alloys are becoming increasingly complex, made up of many different metallic elements at similar concentrations rather than just one or two major elements and a few minor ones. In a recent study, Leroy used EPMA to investigate how the microstructure of a high-entropy alloy comprising chromium, manganese, iron, cobalt and nickel responded to thermal processing. He has also used EPMA to optimize the properties of intermetallic magnesium-lead-copper (MgPdCu) alloys that are essential for hydrogen storage in new battery research and development.¹

‘The major information obtained by EPMA is the precise chemical composition and the X-ray maps,’ says Leroy. ‘Sometimes I also use EPMA for the characterization of multi-layered 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.² This helped to reveal how the environmental conditions on the islands have changed over the past 6500 years. He has also used EPMA to study how the



Copper precipitates in an Mg-Pd matrix. The high-resolution X-ray maps illustrate the microstructure and the composition of the phases in this ternary alloy

*long-term use of self-cleaning glass affects its chemical composition, particularly whether the outer coating of titanium dioxide is prone to leaching away.*³

1. Ponthieu M, Fernández JF, Cuevas F, *et al.* Thermodynamics and reaction pathways of hydrogen sorption in $Mg_6(Pd, TM)$ (TM = Ag, Cu and Ni) pseudo-binary compounds. *Int J Hydrogen Energy* 2014;39:18291–301. (<http://dx.doi.org/10.1016/j.ijhydene.2014.09.034>)
2. Wirmann 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. (<http://dx.doi.org/10.1016/j.quascirev.2011.10.003>)
3. Chabas A, Alfaro S, Lombardo T, *et al.* Long term exposure of self-cleaning and reference glass in an urban environment: a comparative assessment. *Build Env* 2014;79:57–65. (<http://dx.doi.org/10.1016/j.buildenv.2014.05.002>)

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 wrong 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 line up the WDS on the specimen.

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 vapour molecules from interfering with the electron beam. The accelerating voltage and electron beam current then need to be carefully selected and the electron beam 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.

FEGs 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

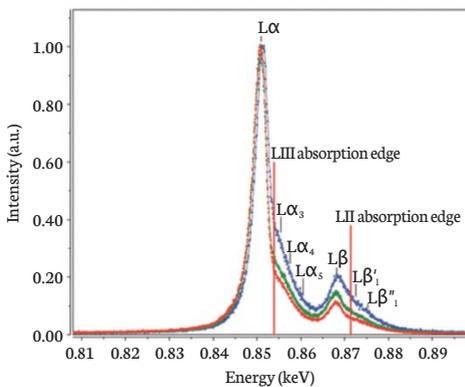


Figure 5. Ni L α L β spectral range in pure nickel acquired at 5keV (blue), 10keV (green) and 15keV (red) revealing modification in shape and peak positions

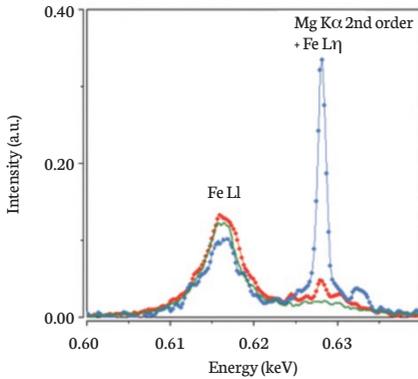


Figure 6. Fe L1 spectral range in pure iron (green), haematite (red), and almandine (blue) allowing accurate quantification of the first series transition metals

quantification with low-energy X-rays can be achieved by using L1 lines (Figures 5 and 6, and see *Case Study 3*).

Challenges specific to quantitative analysis

The parameters that are important to optimize when conducting trace analysis include beam conditions, spectral 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. For example, with an optimized tungsten filament EPMA system, beam stability of $\pm 0.05\%$ per hour can be achieved using permanent beam regulation.

Both trace and quantitative analyses with EPMA are reliant on the multiple WDS 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 on both sides of the peaks.

CASE STUDY 3

Dr John Fournelle at the University of Wisconsin, Madison, USA, has used field-emission EPMA to analyze samples of lunar surface deposits (regolith grains) collected during an Apollo mission. These scarce iron-silicon (Fe-Si) grains are thought to have formed in the reducing environment of the moon after micrometeorite impacts, perhaps affected by solar wind.

Making matters difficult is the fact that the Fe-Si compounds of interest are under one micrometer in diameter, requiring a highly focused, low-voltage electron beam. Before the advent of field-emission sources, there was little research interest in quantitative low-voltage EPMA because the electron beam simply could not be focused to sufficiently small diameters. Also, the related lower electron beam energies mean that many of the inner shell electrons generally used in EPMA cannot be ionized. Because surface contamination can negatively impact results at low voltages, electron probes with oil-free vacuum systems are essential, as well as anti-contamination devices.

Armed with a field-emission probe, however, Fournelle and his team were keen to measure previously poorly studied L shell X-ray lines in the lunar Fe-Si samples, taking advantage of a sub-micrometer beam focusing at low keV. Whereas EPMA normally uses a 15-20keV beam, Fournelle's team was able to use a 5keV beam. 'We quickly found, however, that using the Fe $L\alpha$ or $L\beta$ lines produced incorrect compositions in the reference materials we started experimenting with, before we turned the electron beam loose on the sub-micron lunar grains,' he says.

The researchers discovered that a normally ignored, non-traditional X-ray line, the Fe Ll line, isn't impacted by the complex

phenomenon of self-absorption that affects the Fe L α and L β lines, and thus could produce excellent EPMA results.¹ When Fournelle and his team conducted their original work, no commercial software was available to acquire and process the Fe L α lines. ‘We have been working together with CAMECA, and they have quickly grasped the importance of these non-traditional lines for low-voltage EPMA and have now implemented the utilization of the L α lines in their calibration, measurement and quantification software,’ Fournelle explains. His next objective is to use ‘non-traditional’ M lines for low-voltage EPMA of rare earth elements, a hot topic in both geoscience and materials research.

1. Gopon P, Fournelle J, Sobol PE, Llovet X. Low-voltage electron-probe microanalysis of Fe-Si compounds using soft X-rays. *Microsc Microanal* 2013;19:1698-708. (<http://dx.doi.org/10.1017/S1431927613012695>)

WHAT'S NEXT?

As highlighted in the *History and Background* chapter, 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 such as FEG and the ease of use provided by the latest software tools. Nevertheless, there is still a certain amount of room for improvement.

In particular, 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 (Figure 7).

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

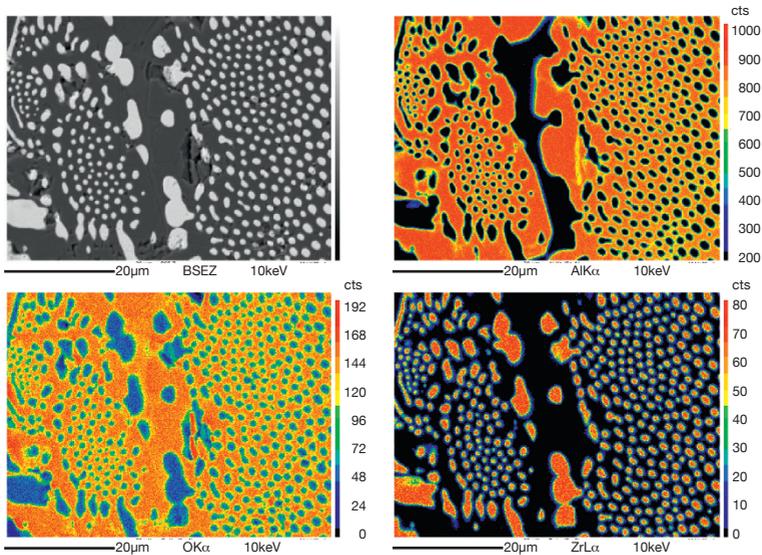


Figure 7. High-magnification X-ray maps acquired on a ceramic specimen illustrating the ability of FEG-EPMA to analyze light elements (oxygen in this case) in a complex ceramic matrix also containing zirconium and aluminium

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 (see *Case Study 4* for another example).

CASE STUDY 4

‘We use EPMA for non-standard things,’ says Professor Robert Martin, a physicist at the University of Strathclyde, Glasgow, UK. His team specializes in the light-emitting semiconductors used in lasers and light-emitting diodes (LEDs), and has recently developed a novel EPMA-based approach for studying LEDs in situ.

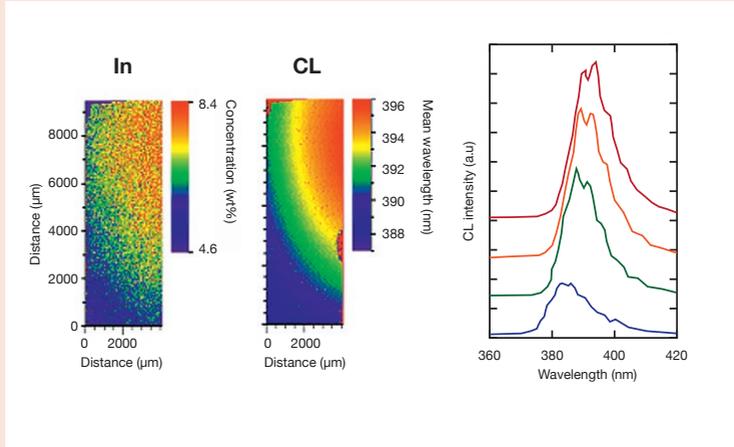
The team originally had to use different instruments to measure semiconductor composition and light emission. ‘We realized that the microprobe allowed you to do both together on a very small region of a sample,’ recalls Martin. Using EPMA, they can now map semiconductors with sub-micrometer scale resolution, simultaneously measuring optical emission spectra and X-ray spectra for elements such as the all-important indium and gallium.¹

Martin’s team uses a CAMECA EPMA, which it has customized by adding its own CL system. The physicists map composition and optical properties and then look for correlations between the two, for example whether the emission becomes brighter with higher concentrations of a particular element.

In addition, Martin’s team has added electron-beam induced current (EBIC) mapping into the mix, allowing them to study semiconductor conductivity at the same time as its elemental composition and optical properties. The electrons and holes generated by electron beam excitation are used to generate conductivity maps, showing how well the charge flows to an external circuit such as that formed using the contacts on an LED.

The physicists originally used EPMA to study specific layers in LEDs, but they have recently taken their approach to new levels by examining finished devices under operation. ‘We realized that

we could take electrical connections into the EPMA chamber and measure operating devices,' explains Martin. 'Recently, we have demonstrated a combination of four techniques (WDS, CL, EBIC and electroluminescence) on the same area of an operating LED.'



Large area composition and CL maps of AlInGaN sample grown at 595°C. Right: CL spectra extracted from the CL map corresponding to four different points. Adapted from Bejtka *et al*²

1. Taylor E, Fang F, Oehler F, *et al*. Composition and luminescence studies of InGaN epilayers grown at different hydrogen flow rates. *Semicond Sci Technol* 2013;28:065011. (<http://dx.doi.org/10.1088/0268-1242/28/6/065011>)
2. Bejtka K, Edwards PR, Martin RW, *et al*. Composition and luminescence of AlInGaN layers grown by plasma-assisted molecular beam epitaxy. *J Applied Phys* 2008;104:073537. (<http://dx.doi.org/10.1063/1.2993549>)

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 50 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 50 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/literature/scientific-publications/epma.aspx>)

Castaing R. *Application of electron probes to local chemical and crystallographic analysis*. PhD Thesis, University of Paris, 1951 English translation by Duwez P and Wittry DB, California Institute of Technology, 1955. (<http://www.microbeamanalysis.org/history/Castaing-Thesis-clearscan.pdf>)

Goldstein J, Newbury DE, Joy DC, *et al.* *Scanning electron microscopy and X-ray microanalysis*, 3rd edn. New York: Springer, 2003. (<http://dx.doi.org/10.1007/978-1-4615-0215-9>)

Holton I. Is energy-dispersive spectroscopy in the SEM a substitute for electron probe microanalysis? *Micros Anal* 2012;26:S4-7. (http://www.microscopy-analysis.com/sites/default/files/magazine_pdfs/magazine%202012_May_Holton.pdf)

Hombourger C, Outrequin M. Quantitative analysis and high-resolution X-ray mapping with a field emission electron microprobe. *Micros Today* 2013;21:10-5. (<http://dx.doi.org/10.1017/S1551929513000515>)

