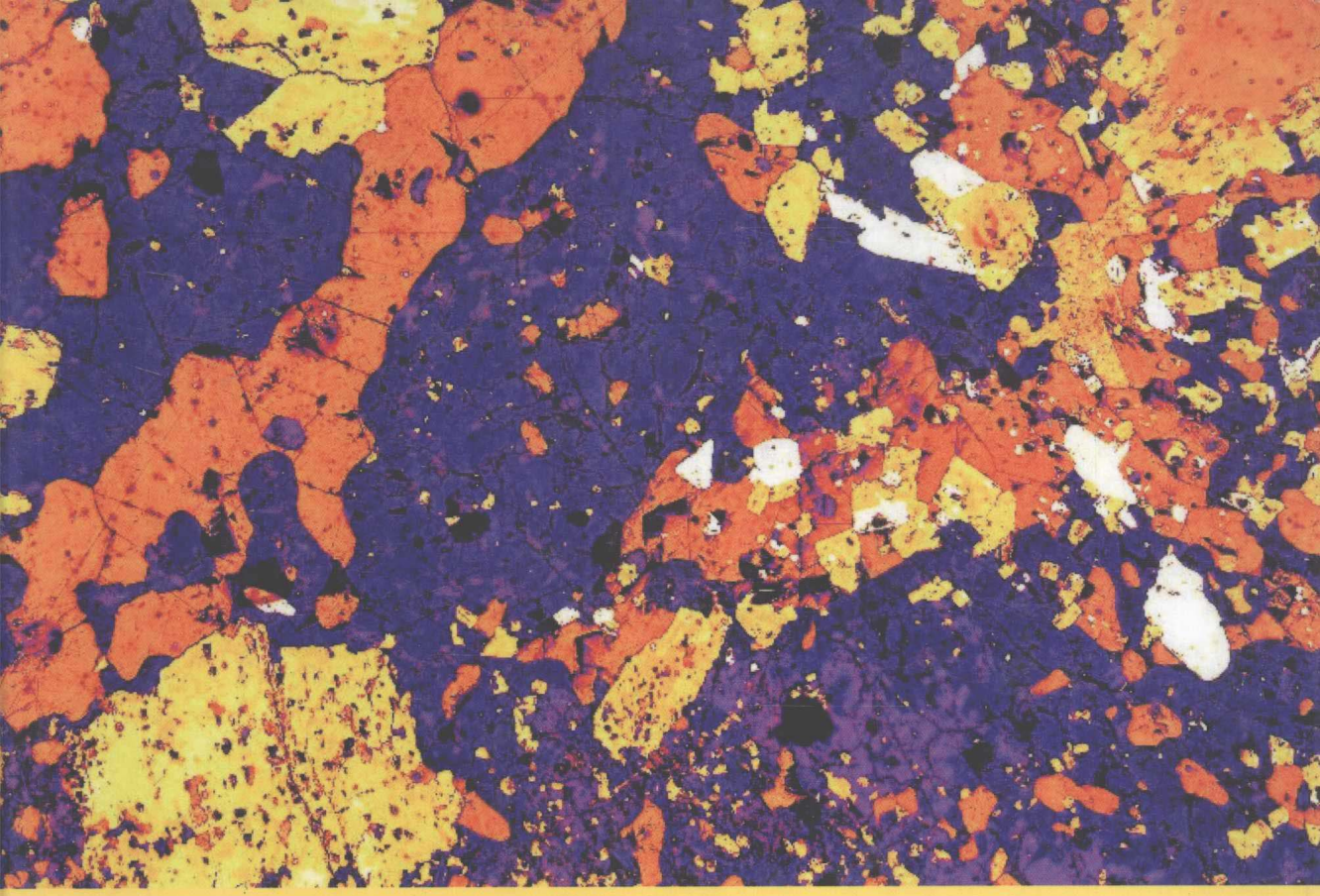
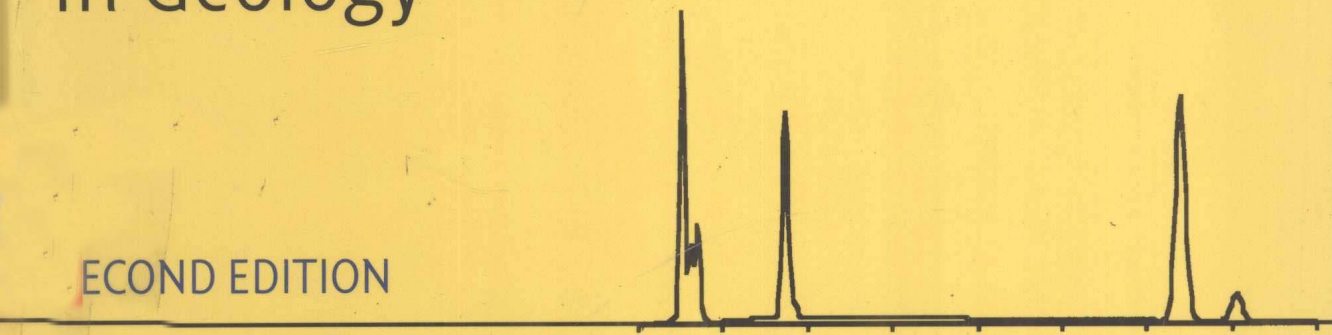


Electron Microprobe Analysis and Scanning Electron Microscopy in Geology

ECOND EDITION



S. J. B. Reed

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Preface

The favourable reception given to the first (1996) edition of this book suggests that the joint treatment of electron microprobe analysis (EMPA) and scanning electron microscopy (SEM) with a specifically geological slant has been found to serve a useful purpose. It was therefore decided to proceed with this second, revised and updated, edition. The inclusion of both EMPA and SEM can be justified on the grounds that the instruments share much in common and their functions overlap: SEMs fitted with X-ray spectrometers are often used in analytical mode, while EMP instruments, though designed primarily for analysis, also have imaging functions similar to those of the SEM.

The capabilities of the computers used both for instrument control and for data processing have increased greatly since the first edition. Whilst this allows more sophisticated software functions, it does not diminish the need to understand both the operating principles of the instruments and the factors controlling the results, the explanation of which is the main purpose of this book. Digital rather than analogue imaging is now the norm, with concomitant advantages provided by image processing and image analysis techniques. The increasing use of 'false' colour images in various forms is reflected in an expanded colour section in this edition. Significant instrumental developments include the increasing adoption of field emission electron sources, which are especially beneficial for high-resolution SEM applications. Also, variable-pressure or environmental SEMs are more commonly used. In addition, interest in ancillary techniques such as cathodoluminescence and electron backscatter diffraction has grown.

As before, no prior knowledge is expected of the reader and technical detail is limited to that needed for a sound understanding of operating principles and interpretation of results. It is hoped that the book will be particularly useful to

postgraduate students and postdoctoral researchers in university geology departments, where it may serve as an accompaniment to courses for SEM and EMPA users.

Inevitably a book reflects the bias of the author and for this I ask the reader's indulgence, as well as for any errors or omissions.

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On a personal note, I would like to record my indebtedness to Jim Long (1926–2003), who played a pivotal role in the development of EMPA in Britain, and whose knowledge and wisdom are greatly missed.

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1

Introduction

1.1 Electron microprobe analysis

Electron microprobe analysis (EMPA) is a technique for chemically analysing small selected areas of solid samples, in which X-rays are excited by a focussed electron beam. (The term 'electron probe microanalysis', or EPMA, is synonymous.) The X-ray spectrum contains lines characteristic of the elements present; hence a qualitative analysis is easy to obtain by identifying the lines from their wavelengths (or photon energies). By comparing their intensities with those emitted from standard samples (pure elements or compounds of known composition) it is also possible to determine the concentrations of the elements quantitatively. Accuracy approaching $\pm 1\%$ (relative) is obtainable and detection limits down to tens of parts per million (by weight) can be attained. Under normal conditions, spatial resolution is limited to about 1 μm by the spreading of the beam within the sample. The spatial distributions of specific elements can be recorded in the form of line profiles or two-dimensional 'maps', which are commonly displayed using a 'false' colour scale to represent elemental concentrations.

1.2 Scanning electron microscopy

The scanning electron microscope (SEM) is a close relative of the electron microprobe (EMP) but is designed primarily for imaging rather than analysis. Images are produced by scanning the beam while displaying the signal from an electron detector on a TV screen or computer monitor. By choosing the appropriate detection mode, either topographic or compositional contrast can be obtained. ('Composition' here refers to mean atomic number: individual elements cannot be distinguished.) Spatial resolution better than 10 nm in topographic mode and 100 nm in compositional mode can be achieved, though

in many applications the large depth of field in SEM images (typically at least 100 times greater than for a comparable optical microscope) is more relevant than high resolution. An important factor in the success of the SEM is that images of three-dimensional objects are usually amenable to immediate intuitive interpretation by the observer. The range of applications of SEM can be extended by adding other types of detector, e.g. for light emission caused by electron bombardment, or cathodoluminescence (CL).

1.2.1 Use of SEM for analysis

Scanning electron microscopes commonly have an X-ray spectrometer attached, enabling the characteristic X-rays of a selected element to be used to produce an image. Also, with a stationary beam, point analyses can be obtained, as in EMPA. (The spatial resolution with respect to analysis is, however, still limited to about 1 μm by beam spreading, despite the higher resolution obtainable in scanning images.) Since EMP instruments have electron imaging facilities, used primarily for locating points for analysis, the functions of the two instruments overlap considerably. The SEM is optimised for imaging, with analysis as an extra, whereas in the EMP the priorities are reversed and various additional features that facilitate analysis are incorporated.

1.3 Geological applications of SEM and EMPA

The advantages of the SEM as an imaging instrument (high spatial resolution, large depth of field, and simple specimen preparation) make it an invaluable tool in the following branches of geology.

Palaeontology. The SEM is ideally suited to the study of fossil morphology, especially that of micro-fossils.

Sedimentology. Three-dimensional images of individual sediment grains and intergrowths can be obtained; data on fabric and porosity can also be generated.

Mineralogy. The SEM is very effective for studying crystal morphology on a micro-scale.

Petrology. The ability to produce images of polished sections showing differences in mean atomic number is very useful both in sedimentary and in igneous petrology.

The reasons for the widespread application of EMPA to geology (whether carried out in a 'true' EMP instrument or in a SEM with X-ray spectrometer fitted), especially in the fields of mineralogy and petrology, can be summarised as follows.

(1) Specimen preparation is straightforward and entails the use of existing techniques of section-making and polishing with only minor modifications.
(2) The technique is non-destructive, unlike most other analytical techniques.
(3) Quantitative elemental analysis with accuracy in the region of ±1% (for major elements) can be obtained.
(4) All elements above atomic number 3 can be determined (with somewhat varying accuracy and sensitivity).
(5) Detection limits are low enough to enable minor and trace elements to be determined in many cases.
(6) The time per analysis is reasonably short (usually between 1 and 5 min).
(7) Spatial resolution of the order of 1 μm enables most features of interest to be resolved.
(8) Individual mineral grains can be analysed *in situ*, with their textural relationships undisturbed.
(9) A high specimen throughput rate is possible, the time required for changing specimens being quite short.

These characteristics have proved useful in the following subject areas.

Descriptive petrology. The EMPA technique is commonly used for the petrological description and classification of rocks and has an importance comparable to that of the polarising microscope.

Mineral identification. As an adjunct to polarised-light microscopy and X-ray diffraction, EMPA provides compositional information that assists in mineral identification.

Experimental petrology. For experimental studies on phase relationships and elemental partitioning between coexisting phases, the spatial resolution of the electron microprobe is especially useful, given the typically small grain size.

Geothermobarometry. The EMPA technique is ideally suited to the determination of the composition of coexisting phases in rocks, from which temperatures and pressures of formation can be derived.

Age determination. Th–U–Pb dating of minerals containing insignificant amounts of non-radiogenic Pb (such as monazite) is possible by EMPA, with higher spatial resolution than can be obtained with isotopic methods, though lower accuracy.

Zoning. The high spatial resolution of the technique enables zoning within mineral grains to be studied in detail.

Diffusion studies. Experimental diffusion profiles in geologically relevant systems can be determined with the electron microprobe, its high spatial resolution being crucial in this field.

Modal analysis. Volume fractions of minerals and other data can be obtained by automated modal analysis, mineral identification being based on X-ray and sometimes backscattered-electron signals.

Rare-phase location. Grains of rare phases can be located by automated search procedures, using the X-ray signal for one or more diagnostic elements.

1.4 Related techniques

Though EMPA has many useful attributes, as described in the previous section, other, complementary analytical methods offer advantages in one respect or another. These are outlined briefly in the following sections.

1.4.1 Analytical electron microscopy

With specimens less than 100 nm thick and an electron energy of at least 100 keV, much better spatial resolution (down to 10 nm) can be obtained, owing to the relatively small amount of lateral scattering which occurs as the electrons pass through the specimen. The reduction in X-ray intensity can be compensated to a large extent by using an X-ray detector of high collection efficiency and a high-intensity electron source. This type of analysis can be carried out in an 'analytical electron microscope' (AEM), in which conventional electron transmission imaging and diffraction capabilities are combined with X-ray detection. Analysis with high spatial resolution is also possible with a scanning transmission electron microscope (STEM) fitted with an X-ray spectrometer.

Another analytical technique that is also available in AEM and STEM instruments is electron energy-loss spectrometry ('EELS'), which utilises steps in the energy spectrum of transmitted electrons caused by energy losses associated with inner-shell ionisation. Electron spectrometers with parallel collection make this a very sensitive technique.

For further information about AEM, see Joy, Romig and Goldstein (1986) and Champness (1995).

1.4.2 Proton-induced X-ray emission

Characteristic X-rays can be excited by bombardment with protons, giving rise to the technique known as 'PIXE' (proton-induced X-ray emission). The principal advantage of PIXE is that the X-ray background is much lower than in EMPA (a consequence of the higher mass of the proton compared with the electron), making small peaks easier to detect. Detection limits are thus typically an order of magnitude lower (in the ppm range). On the other hand, high-energy protons are more difficult to focus in order to obtain high spatial resolution (a beam diameter of 1 μm is attainable, but only with low current), and they penetrate much further in solid materials. Protons of energy 1–4 MeV, which give efficient X-ray excitation, can penetrate the full 30-μm thickness of a petrological thin section and it follows that the spatial resolution

with respect to *depth* is relatively poor. The equipment is quite costly and not very widely available, so geological applications have been fairly limited.

For more details about PIXE, see Fraser (1995), Halden, Campbell and Teesdale (1995) and Cabri and Campbell (1998).

1.4.3 X-ray fluorescence analysis

An alternative way of exciting characteristic X-rays is to bombard the specimen with X-rays of higher energy, this technique being known as X-ray fluorescence (XRF) analysis. It has been a standard method of elemental analysis in geology for a long time and offers good accuracy for major elements and detection limits in the region of 1 ppm. In its usual form it is a bulk method, requiring a significant amount of sample for analysis, and is therefore used principally for analysing whole rocks or separated minerals. An electron microprobe or SEM can, however, be converted to make it capable of XRF analysis with a spatial resolution of about 100 μm, by using the beam to excite X-rays in a target close to the specimen, in which fluorescent X-rays are excited.

The advent of synchrotron X-ray sources has revolutionised the possibilities of XRF analysis. The extremely high X-ray intensities available from these sources enable intense beams down to 1 μm in diameter to be produced for exciting the specimen, giving a microprobe technique in which high spatial resolution and low detection limits are combined. The accessibility of this technique is restricted by the limited number of synchrotrons in existence. For more information, see Smith and Rivers (1995). Relatively compact XRF analysers with high spatial resolution, using a low-power X-ray tube with a focussing device, are also available.

1.4.4 Auger analysis

The process known as the 'Auger effect', whereby an atom excited by electron bombardment may dissipate its energy by ejecting an electron rather than by characteristic X-ray emission, gives rise to an alternative method of analysis, which exploits the fact that the electron spectrum contains lines that have energies related to the atomic energy levels and are therefore characteristic of the element. Auger analysis is most effective for elements of atomic number below 10, for which X-ray analysis is least sensitive. Also, it differs in being a surface analysis technique, only electrons originating from depths of the order of 10 nm being detected. The scanning Auger microscope (SAM) is a close relative of the SEM, but is orientated towards the requirements of the