Chapter One

An introduction to scanning electron microscopy and electron probe microanalysis

1. Introduction

As scientists, our view of the universe is more often than not from a *macro*scopic perspective. At this stage in your education, you are certainly aware that cosmology, astronomy and geology, as "historical" fields of investigation, rely heavily upon the other sciences since these fields encompass phenomenon that cannot be experimentally repeated; at least not easily or at full scale. In order to fully appreciate the structure and dynamics of the natural universe, we must have a good understanding of physics and chemistry. In order to understand our place on this planet, we've come to recognize the importance of the life sciences. And, at the most basic level, we must appreciate mathematics and the relatively new discipline of computer science. To get this far up the ladder of scientific training, you have undoubtedly been introduced to many tools with which we measure, test and view our surroundings. In this course you will be introduced to a powerful new generation of instruments designed to provide both qualitative and quantitative information from a *micro*scopic perspective. Electron-beam instruments have become some of the most powerful and versatile tools for understanding contemporary problems in the Earth and Materials Sciences. We hope you will appreciate this course because electron microscopy and electron microanalysis are fascinating techniques, and because they tend to produce more interesting questions than they answer. The course will not simply be a training workshop. Through reading, lectures and lab sessions we will review and introduce principles of chemistry, physics, mathematics and computer science. Our philosophy is that the more you know about electron-beam instruments and of electron - specimen interactions, the more efficiently you will be able to utilize the instruments, more intelligently interpret the data or imagery, and thereby produce high quality results that you can defend with rigor and confidence.

We have all been exposed to the marvelous photographs of insect heads and bodies produced with a scanning electron microscope (SEM). These micrographs, while imaging something smaller than a *speck*[1], with electrons rather than light, make microscopic features appear as part of our own world. National Geographic's, *A Small World*, (PBS television) is an

[1] Defined as detectable by the eye, but without detail; approximately 0.1mm.

excellent exposé for the layman, although fearfully revealing of the many parasites that live on the human body. In geology and material science, the SEM has provided high resolution images of objects too small to be properly studied with an optical microscope. These applications of interest to range from the identification of micro-fossils (figure 1-1) to the study of nanoscale devices.

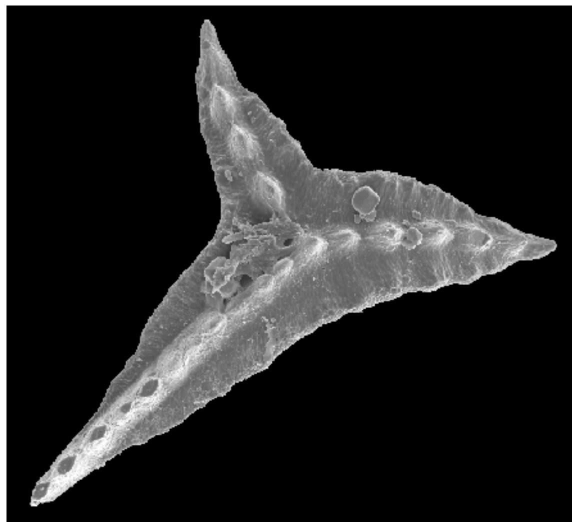

Figure 1-1 SEM micrograph of conodont micro-fossil. Horizontal scale is 1mm (Ancyrognathus amplicavus courtesy of Norm Savage)

Electron probe microanalysis (EPMA) is a quantitative technique with which it is possible to measure the fractional concentration of almost any element in a solid material. It is called a micro-technique because the volume analyzed can be as small as one spherical micron[2] and even smaller at low energies. If we consider the density of a typical material this volume translates into approximately a trillionth of a gram (10^{-12}gm). Considering the sensitivity of the technique, which can be approximately 100 ppm for many elements, EPMA can sample one ten-thousandth of a trillionth of a gram (10^{-16}gm). With an analytical precision of less than 2% relative for major elements, EPMA is clearly one of the most versatile tools for solving a wide variety of geological or material science problems.

The EPMA technique is not limited to micro-specimens. The most common applications involve measuring elements of interest in a micro volume within a larger volume, e.g., analysis of an inclusion within a mineral grain within. Specimens can be relatively large, many EPMA instruments can accommodate specimens as large as 100mm in diameter. The analysis need not be quantitative either; for example, for many research problems all that need be determined is how an element's abundance varies from core to rim. Is it more or less? Is the variation sinusoidal? Is it a saw-tooth variation? Which way does the saw-tooth vary? (Figure 1-2)

Figure 1-2 Qualitative elemental distributions along a line (line scan). (a) sinusoidal; (b) sawtooth; (c) complimentary sawtooths for two elements.

Newer EPMA instruments allow

2 One micron (μm) is one millionth of a meter.

qualitative compositional variations to be determined in two dimensions, in the form of *elemental* or *x-ray dot maps* (Figure 1-3). Although these data acquisitions are time consuming, the results can be extremely informative and are easily interpreted by the human eye. In many instances the microprobe has identified new minerals or materials with novel properties, and more fully characterized previously known substances. In this role, EPMA has made major contributions in chemistry, physics and terrestrial as well as meteorite and lunar mineralogy. Petrology, which is the study of mineral assemblages and their genesis, has taken major leaps forward since the advent of the electron microprobe. Exsolution lamellae, small inclusions and mineral zoning profiles, while only evident with a petrologic microscope, can be quantitatively analyzed.

Let us conclude this brief introduction with a quote from one of the better-known petrologists, Klaus Keil. His message, which appears in a text edited by C.A. Anderson (see bibliography), is dated but the message is still appropriate.

> *"In the earlier days of electron microprobe analysis, only limited use was made of the instrument by geologists: in 1964, 14 years after the invention of the electron microprobe, only about 60 papers had been published which dealt with the application of the instrument to geology, more than half of which were devoted to meteorite research and related topics. Since then, and at the time of this writing (May, 1971), more than 600 papers have appeared in the literature dealing with the electron microprobe and its application as a major research tool in mineralogy, petrology, geochemistry, meteorics, and related disciplines. Most major geology departments and many government laboratories in this country and abroad now make extensive use of the instrument, and several departments offer graduate courses on electron microprobe analysis with special reference to the earth sciences. It may be said that, in recent years, no other research tool has revolutionized geology as much as the electron microprobe, and its impact on the earth sciences can only be compared to the introduction of the polarizing microscope to geology more than 125 years ago. In spite of the extensive ongoing research in this field, we are still at the beginning stages of a new epoch in geology and much remains to be done in the future."*

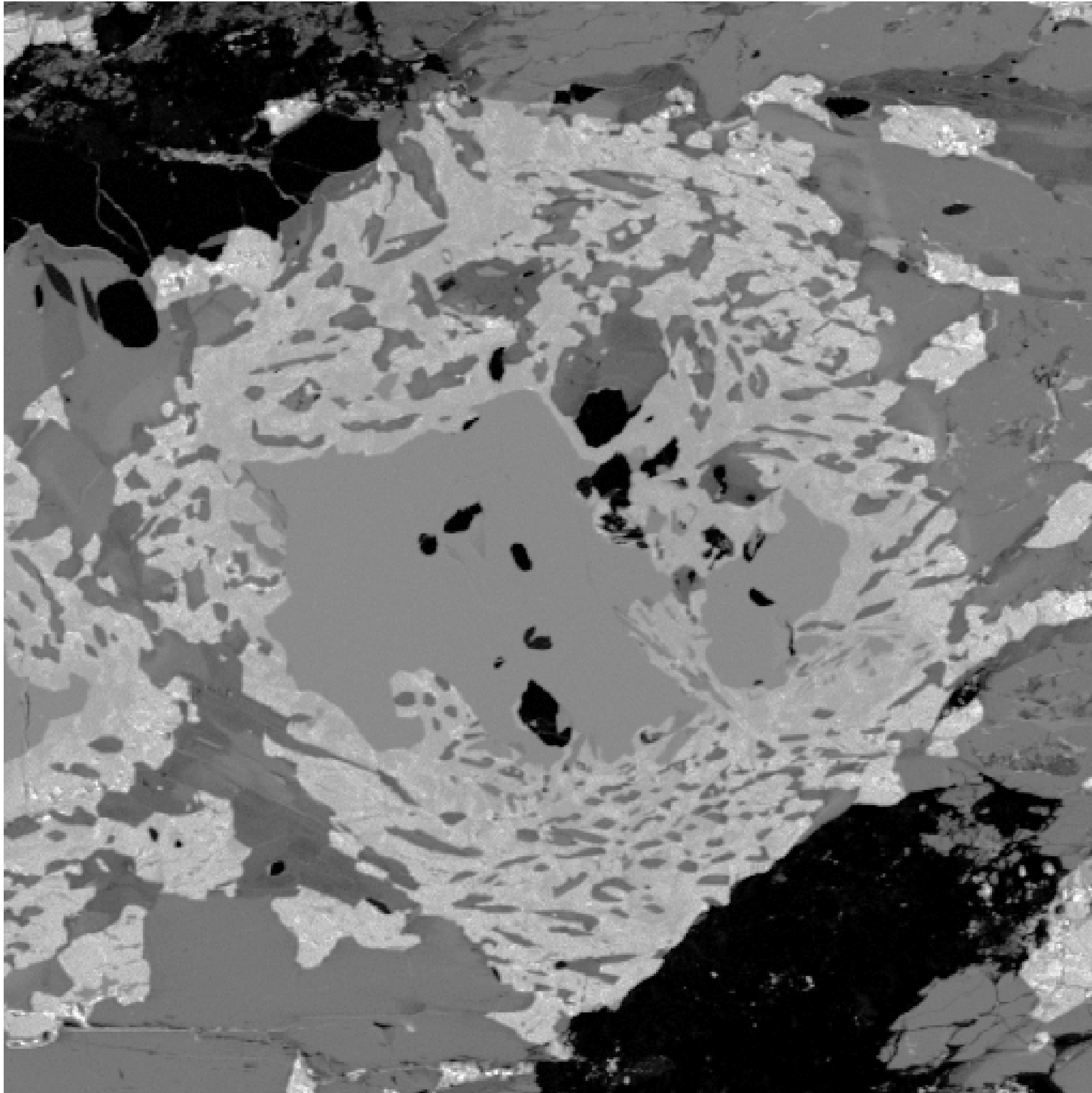

Figure 1-3 An elemental map of the spatial distribution of aluminum for feldspar replacing garnet. Note the once euhedral outline of the pre-existing garnet.

1.1 Evolution of the scanning electron microscope.

The SEM and EPMA belong to a general family of particle beam instruments that utilize high-energy electrons and the information gained from their interaction within a specimen. Because the electron microprobe can be considered to be a big brother to the scanning electron microscope[3] we begin with a brief history of electron microscopy.

It has been long recognized that electrons as charged particles can be accelerated within a vacuum, focused onto a small spot of target material where they interact with other electrons and/or the atoms or molecules within the specimen being bombarded. The first electron microscopes were constructed during the early part of the 20th century. The B&W film "The Man in the White Suit" with Alec Guiness is a very funny film, that includes an early electron microscope as a prop. These instruments were confined to the study of thin specimens and the electron deflections that took place as the primary electrons passed through the thin specimen. The electrons that were transmitted through the specimen were recorded directly on photographic plates, and thus revealed the specimen's internal structure. Today this type of microscope is specifically termed a ***transmission electron microscope (TEM)***. TEMs can utilize extremely high voltages (100,000 to 5,000,000 volts) and are capable of imaging a crystallographic lattice containing large atoms or molecules. Credit for the first *scanning microscope* is sometimes given to von Ardenne, who in 1938 first applied electrostatic scanning coils to a TEM. The term *scanning* refers to viewing an indirect signal on a CRT whose rastering scan rate is synchronized with the scan rate of the electron beam on the target. Von Ardenne's instrument passes the minimum criterion for an SEM; however, today his type of instrument is specifically known as a ***scanning transmission electron microscope (STEM)***, and is still often used in material science research. Current STEM instruments with electron beam monochromators, spherical abberation correctors and high speed computer processing methods are capable of imaging single atoms in an atomic lattice in real time. If the STEM is also equipped with quantitative capabilities, it is termed an ***analytical STEM***. SEMs, as they are defined today, are designed around a later discovery, usually attributed to Zworykin and Hillier (1942). Their primary discovery was the production and detection of *secondary electrons*, which are emitted from a specimen subsequent to the interaction with the probe's primary electrons with the specimen. Secondary electrons (SE) have only enough energy such that emission only from the surface of a specimen is possible, hence the information gained is not dependent on electron transmission. At this point in history it was realized that just about any material could be examined with energetic electrons with a minimum of specimen preparation. The SEM today relies on the SE detector as its primary source of information to send to the viewing and photo CRTs.

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[3] The first microprobe was a modified electron microscope, and many microprobes today are SEMs with elemental detectors simply added, although strictly speaking a microprobe has a coaxial light optics system for accurate z-axis stage positioning to avoid bragg defocussing of the wavelength dispersive x-ray optics

Conceptually, today's SEM hasn't changed much except for refinements that have minimized the size of the spot[4] on which the primary electrons are focused, and in the sensitivity of the detectors. Zworykin *et al*. can also be given credit for a brighter source for the primary electrons (cold cathode field emission), a photomultiplier for pre-amplifying the SE signal, and the first detailed analysis of the interrelationship of gun brightness, lens aberrations and spot size. Their SEM was able to achieve a resolution (spot size) of 50 nanometers[5], ... in 1942!

Owing to the demands of the war, work on fully developing the instrument didn't continue until 1948, when researchers at Cambridge (UK) took up the task. However, Oatley and McMullan were not able to duplicate Zworykin's accomplishments until 1952. K.C.A. Smith (1956) followed their work, improved the signal processing, replaced the electrostatic components with electromagnetic devices, and added a stigmator to correct inherent astigmatism. T.E. Everhart and R.F.M. Thornley (1960) modified the SE detector for a much more improved signal. By intimately connecting the primary scintillator and light tube to the photomultiplier, small contrast mechanisms could then be recognized. This type of SE detector is still the standard for all instruments today, and is known as the Everhart-Thornley type detector.

Since the late 1940s, prototypes continued to be made in just about every industrial country. However, it wasn't until the 1960s that commercial manufacturing and distribution took place under the guidance of A.D.G. Stewart (1965), and with the groundwork laid out by R.F.W. Pease and W.C. Nixon (1963,1965). Cambridge Scientific Instruments succeeded in making the SEM commonplace in many aspects of research during that era (and continues to do so today).

Continuation of this overview of the instrument's history is difficult because of the number of contributions and credits which would exclude the degree of collaboration, and because most refinements were attributable to the manufacturers. Whereas the common source for primary electrons continues to be a thermionic tungsten filament, cold cathode field emission was further developed, as well as thermionic lanthanum hexaboride, both of which offer several orders of magnitude improvement in gun brightness. Improvements in signal processing attributable to development in other types of instrumentation were applied to SEM image processing. Backscattered electrons (BSE), capable of imaging atomic number contrast, were successfully discriminated from the specimen emission and made sensitive enough such that BSE detectors are now commonplace, and are used complimentary with both the SE signal and x-ray information from the specimen.

Most recently, microcomputers have been integrated into the electronic systems of all modern SEMs. Computer keyboards have largely replaced analog control knobs for adjusting

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[4] The size of the electron beam on the specimen is commonly referred to as *resolution* and has much to do with the capabilities of the SEM’s effective magnification.

[5] One nanometer (nm) is one thousandth of a micron, or one millionth of a millimeter.

instrumental parameters, acquisition of images and processing of images. Today these computer digital images today easily rival and often exceed the quality of traditional photo-emulsion photography. Not only are they much more convenient for many applications (e.g., journal publication) they are less harmful to the environment (no photographic chemicals or silver) and also more energy efficient than typical photographic and darkroom techniques.

1.2 Evolution of the electron probe microanalyzer .

> *"In January 1947, I joined the Materials Department of the Office National d'Etudes et Recherches Aéronautiques (ONERA), in a little research center 30 miles away from Paris, near the village of Le Bouchet. My laboratory was equipped with an ill-assorted collection of scientific apparatus, most of which had been obtained from Germany at the end of the war; but in December I received the basic equipment I had been promised when engaging at ONERA: two electron microscopes, at the time a real luxury. One of them was a French electrostatic instrument manufactured by the C.S.F.; the other an R.C.A. instrument; it was very pretty indeed and I was fascinated - I am ashamed to say - by the American technology. I used that microscope, together with the oxide replica technique, for studying the wonderful arrangements of oriented precipitates - platelets or needles - which form when light alloys are annealed at moderate temperatures. That was the occasion for me to meet Professor Guinier who studied the same alloys with x-rays in his laboratory at the Conservatoire des Arts et Métiers. I was astonished to learn from him, in the course of one of our conversations, that the composition of most of the precipitates or inclusions which appear in the light micrographs was in fact unknown, in spite of the art of the metallographers, if their number was too small for recognizing the phase by x-ray diffraction. On that occasion he asked me my opinion about identifying at least qualitatively the elements present in such minute individual precipitates by focusing an electron beam onto them and detecting the characteristic x-rays so produced. I replied straight-away that to my mind it was very easy to do; I was surprised that no one had done it before. We agreed that I would try to do the experiment, even if it appeared a little too elementary a subject for a doctoral thesis. In fact, there were some slight difficulties as I was to find out during the next 2 or 3 years."*

The above quotation is Raymond Castaing's introductory paragraph in his monograph, *Early Times in Electron Microprobe Analysis* (Heinrich, 1991). In those 2 or 3 years, Castaing's dissertation research produced the first electron probe microanalyzer; it is a classic dissertation in scientific instrumentation. Together with Dr. Guinier he delivered the technique's first paper in 1949, and by the time his thesis was defended in 1951, he had not only conceptualized EPMA, but had laid the groundwork and accomplished much of the research required to make the technique quantitative. To put this into perspective, our CAMECA SX-50 is the direct descendent of Castaing's Ph.D. dissertation!

Credit for the actual concept should be given to James Hillier (1947), to whom the U.S. patent was awarded. X-rays, at least as energetic radiant energy, had been recognized since before the turn of the century. By the 1920s, researchers were generating x-rays with energetic electrons, and quantitative x-ray spectral analysis had been developed based on H.G.J. Moseley's observation (Figure 1-4) of x-ray energies being characteristic of the material in which they are excited. X-ray tubes which have long been the source for x-rays for medicine (x-ray diffraction, etc.) haven't changed much, and are basically a vacuum tube in which thermionic electrons are accelerated with high voltage towards a target which emits x-rays with a specific (characteristic) energy or wavelength. For example, x-ray tubes for x-ray diffraction, use a copper or nickel target which emit x-rays with a wavelength of 1.54184 or 1.65919 angstroms (Å), respectively. Hillier's idea, and subsequent patent, utilized electrons generated with an electron microscope to qualitatively examine a small area, but took the concept no further. Castaing did the real design work, not only making Hillier's idea a reality, but also made it quantitative.

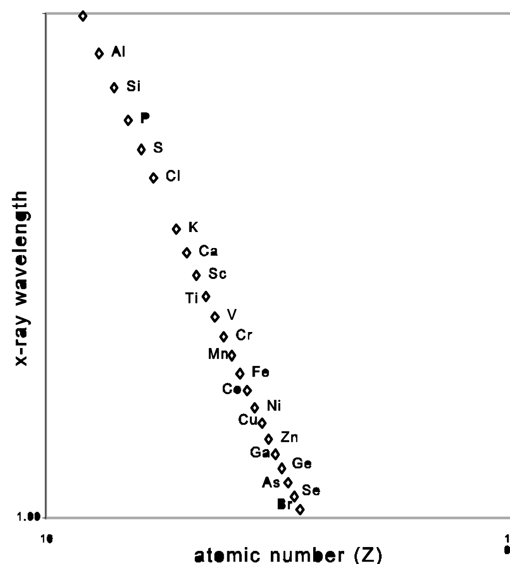

Figure 1-4 Moseley's law

During the 1950s many EPMA prototypes were built by research labs in Europe and the United States (Haine and Mulvey, 1959; Birks and Brooks,1957; Fisher and Schwarts, 1957; Wittry, 1957; Cuthill, Wyman and Yakowitz, 1963). The first commercial instrument was introduced by CAMECA in 1956 based on Castaing's design. Most of the early prototypes utilized a fixed electron beam. Cosslet and Duncumb (1956) made a major contribution by designed the first scanning probe. Their instrument used the backscattered electron signal as its primary image former, which made the technique even more powerful and popular.

Castaing had amplified Hillier's concept by recognizing that if unknown x-ray intensities were measured relative to a pure element, a first approximation could be made towards quantifying the chemical composition of the specimen being bombarded by electrons (inaccuracies in this approximation are taken up later). However, he soon learned how complex the x-ray generation can be in a multi-element specimen -- his thesis was no longer elementary. This complexity is based on unknowns regarding the specimen in which the electron-solid interaction volume varies with composition, as does the extent of absorption in the path for the x-rays leaving the specimen. These complications are now known as the atomic number (Z) and absorption (A) effects. The interaction is further compounded with the fluorescence effect (F), which addresses the possibility of generating secondary x-rays when the primary x-rays are absorbed within the specimen. Castaing laid the groundwork and these complexities were later taken up by Wittry (1963), Philibert (1963), Duncumb and Shields (1966), and are still

researched today for lighter elements such as oxygen and more esoteric x-ray emission lines such as the L and M series.

Instrumental refinements have been progressively developed. Because traditional x-ray spectrometers use a Bragg diffractometer to discriminate characteristic x-rays, the number of elements was limited to those of relatively high atomic number. Newly developed pseudo-crystals with larger d-spacings have allowed measurement of lighter elements, down to oxygen, and nowadays, using multi-layer diffractors, even beryllium. Non-focused spectrometers were replaced with focusing types which increased the x-ray signal and increased the instrumental sensitivity. Electromagnetic lens technology allowed smaller objective lenses that alleviated interference with the path the emitted x-rays take towards the spectrometer.

A solid state detector capable of discriminating x-rays by their energy was devised in the late 1960's. Whereas traditional wave-length discriminating spectrometers (WDX) have to be *tuned* to a suspected and specific x-ray wavelength, the energy discriminating detector (EDX) can measure all x-rays simultaneously and display the spectrum in real time as the number of x-ray counts versus energy[6]. Since qualitative analysis is often a significant part many analyses, this improvement simplified the instrument's use considerably. More than any other refinement, this type of detector has done more towards making EPMA both popular and affordable. EDX detectors are a relatively inexpensive (~$50K) option and found on many SEMs today. Electron probe microanalyzers are, by definition however, designed around WDX spectrometers that are more precise and sensitive by an order of magnitude. Do not confuse EPMA with SEM/EDX, although instrumentally they are similar, as are most of their applications.

As with all scientific instrumentation, the computer has been a major advance. However, because of the nature of inherent after-processing of EPMA data, mundane computation, i.e., corrections to the first approximation, has been a necessity for this instrument from the beginning. In the early days, numerical corrections were done on paper, and consequently were only realistic for very simple specimens. During the 1960s, raw data could be punched onto paper tape or cards by a teletype machine and carried to the local computer housed in the building across campus.[7] Although specimen analysis had increased in complexity, computations were simplified and based on simple models for the sake of computer time. Today is another story; with the desktop computer, the most accurate computational models can be applied to the data from the most complex specimen (e.g., 16 elements in biotite) and even geometric considerations for thin films on substrates. With today's desktop computer in close proximity to the instrument, the analysis can be obtained within seconds. Image

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6 EDX spectra are very useful and easy to evaluate. Because of Moseley's relationship between atomic number and wavelength (and energy), such spectral displays are, in effect, x-ray intensity versus atomic number.

7 This was the case here at the University of Oregon. In 1968, with a NASA grant to analyze lunar samples, raw data from an ARL EMX microprobe was made machine-readable as holes in paper and calculated as weight percent at the original UO Computer Center.

acquisition and processing of elemental maps has also been made possible with the today's computer power. The ability to correlate x-ray maps for many elements simultaneously, allows maps of phases, and subsequent modal analysis of complex rocks and other materials.

1.3 About this text

The following chapters are condensations of many texts and papers, and we refer you to the bibliography for this course. These notes are by no means intended to replace any of these fine texts on electron microscopy and x-ray microanalysis; they are however intended to be less expensive. Quite a bit of the following is taken from Heinrich (1981), which we have found to be the most accurate and comprehensive; unfortunately it is out of print. We value in same regard, Goldstein, et al., *Scanning Electron Microscopy and X-ray Microanalysis* (1984). Please consider, as advanced texts, Newbury, et al., *Advanced Scanning Electron Microscopy and X-ray Microanalysis* (1987), and Heinrich and Newbury (editors), *Electron Probe Quantitation* (1991), the latter being the most up to date, and a very fine collection of monographs written by the *who's who* in electron probe microanalysis. If you go on to utilize either the scanning electron microscope or the electron probe microanalyzer to a significant degree we would advise you to purchase both a comprehensive text and/or one of the advanced texts.

EPMA analyses continue to be the most poorly reported type of analytical measurement. Tables of analyses typically are lacking error estimations or any reference to the computational model used for data reduction. Even within standard texts of mineralogy, mineral analyses are reported to 4 significant figures that are beyond the precision of this technique. As powerful as this analytical technique is, it is only because analysts take care before and during the process, as well as with the interpretation. For example, electron probe microanalyses cannot stand alone; how are elemental concentrations within a specific micro-volume supposed to be interpreted without knowledge of the elemental availability based on some type or macro-analysis? You will, by the end of this course, realize an appreciation for other types of analytical techniques, whether it is whole-rock analysis with atomic absorption, or depth profiling using the TOF-SIMS. It is our hope, by having taken this course, *Electron Probe Microanalysis*, that you will have gained a basis for responsible reporting and meaningful interpretation of your data.

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