

CHAPTER 6

Quantitative Analysis of Minerals

The following topics are covered in this chapter:

- Introduction to the quantitative analysis of minerals*
- Electron microprobe and analytical scanning electron microscope*
- Guiding principles*
- Generation of X-rays*
- Critical excitation energy*
- Beam-sample interactions*
- Quantitative analysis*
- Matrix correction*
- EDS and WDS analysis*
- Characterization of minerals: X-ray powder diffractometer*

ABOUT THIS CHAPTER

The optical identification of minerals is a routine and important procedure in the study of minerals and rocks. However, a critical evaluation of the origins of minerals and rocks requires precise chemical analysis and high-magnification imaging of them. In most modern laboratories, X-ray techniques are routinely used in order to simultaneously obtain high resolution images of individual mineral grains and their chemical compositions. Three most commonly used instruments are the electron microprobe (EMP), the scanning electron microscope (SEM), and the X-ray powder diffractometer (XRD). SEM is primarily suited for the imaging of samples at micron scales and EMP is mainly used for chemical analysis and some imaging. XRD is routinely used to characterize minerals, especially when they are very fine grained.

All modern instruments come equipped with excellent, user-friendly, computer-driven automation systems, which render their operation so simple that only a functional knowledge of these instruments is necessary. In the case of EMP and analytical SEMs, however, the quality of the mineral or material analysis may vary considerably, even with such high level of sophistication. Therefore, the user must have some ways to distinguish between "good" and "bad" analysis. Excellent textbooks and journals on the topic of imaging and analysis are available. This chapter provides only a broad overview of these instruments. Finally, a short section is added on how to evaluate the analyses of common rock-forming minerals.

QUANTITATIVE ANALYSIS OF MINERALS: EMP AND ANALYTICAL SEM

The techniques involved in the chemical analysis of minerals may be grouped into two types: *destructive* and *nondestructive*. In destructive analysis the mineral sample is dissolved in solution or powdered and analyzed for its elemental abundances. Because the

sample must be "destroyed" in such a process, such a technique does not allow detailed analytical study of such important features as zoning in individual mineral grain or reaction zones between grains. Zoning and reaction boundaries between adjacent mineral (or glass and mineral) grains can be examined with a very small electron beam employed in the nondestructive technique in an EMP and a SEM. In most laboratories, the SEM is used for imaging biological and fossil samples. However, in some laboratories, the SEM is fitted with analytical equipment so that chemical analysis of minerals/materials may be obtained. This type of SEM is called an *analytical SEM*.

An EMP or analytical SEM are only capable of analyzing for major (abundance greater than 3 weight%) and minor elements (abundance 0.1–3 wt%). Although some authors have used these instruments to obtain trace element abundances (at parts per million levels), that is not a routine practice. Trace element compositions on single crystals are more commonly obtained with an ion microprobe; and a discussion of this instrument is beyond the scope of this book. An additional handicap of most EMPs and analytical SEMs is that they cannot distinguish between polymorphs with identical chemical compositions. However, this is commonly not a problem because optical mineralogical techniques can usually tell us which polymorph it is. But when the mineral is extremely fine grained, as is the case with clay minerals, X-ray diffraction methods are used to identify a crystalline phase. Most laboratories house an X-ray powder diffractometer (XRD).

The advantages of EMP or SEM analysis are as follows: they are non-destructive; they are extremely rapid; sample preparation is relatively simple, and any well-polished thin section of a rock or a mineral may be analyzed; micron-sized domains within individual mineral grains may be analyzed for major and minor elements with excellent accuracy; with the EMP, a microscope allows viewing of the sample as it is being analyzed; and changing samples is rapid and simple. There are certain things that these instruments are unable to do. They cannot distinguish between valence states of a particular element; for example, the amount of Fe in a mineral analyzed by an EMP is assumed to be in a ferrous state. This often results in a low total in a mineral analysis. This is particularly true of Fe-Ti oxide minerals, which often contain a significant amount of Fe₂O₃ component. The abundance of H₂O, an important constituent of hydrous minerals and glasses, cannot be determined with an EMP.

Since the basic premise of all X-ray techniques is X-ray generation, we first present a brief outline of how X-rays are generated.

X-RAYS AND THEIR GENERATION

X-rays are a type of electromagnetic radiation whose wavelengths fall in the range of 10^{-8} to 10^{-12} meters, which is shorter than the wavelengths of a different type of electromagnetic radiation—visible light (10^{-6} to 10^{-7} m). In the *ground state* of an atom, electrons occupy the lowest energy configuration possible. In SEM or EMP analysis, such an atom within the target mineral is "excited" by knocking off an electron from an inner shell, such as the K shell, with an energetic electron from the beam of electrons generated from the filament of the instrument. That is, the atom becomes ionized. An electron from one of the outer shells drops in to take the place of the missing electron in the K shell in that excited atom. Because the K-shell electron has lower energy than the outer shell electron, this electron transition releases the excess energy in the form of *X-ray photons* (or quanta of energy). The X-rays so produced have wavelengths that are characteristic of the elements present in the mineral. These characteristic X-ray lines are called K α , K β , L α , L β etc. depending upon the orbitals

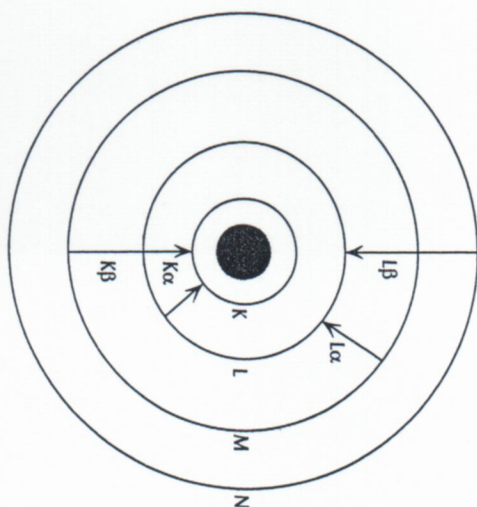


FIGURE 6.1 Electron transitions (indicated by arrows) and the generation of K α , L α , and M α X-rays. (From Goldstein et al., 1992, 2nd ed., *Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Publishers)

involved in the electron transition: for example, when an electron jumps from L to K shell, the excess energy release results in a characteristic line called K α (Figure 6.1).

Inner shell electrons and X-rays typically have energies of several kiloelectron volts (keV). This may be compared to the few electron volts (eV) of energy of light quanta. In generating a characteristic X-ray photon, the incident electron in an EMP or SEM must have sufficient kinetic energy (E_0) that will exceed a certain amount of energy, called the *critical excitation energy* (E_c), of, for example, the K-shell such that it can knock off a K-shell electron. The E_c 's of the X-ray photons depend on the nature of the electron transition.

X-rays behave as both waves and particles (photons). The energy (E) and wavelength (λ) of an X-ray is related by the expression:

$$E\lambda = 12398 \quad [\text{Eq. 6.1}]$$

where E is in electron volts and λ is in Angstrom units (\AA ; $1\text{\AA} = 10^{-10}$ meters).

The basis for a qualitative analysis of elements is the relationship that the E_c of an X-ray "line" (e.g., K α_1) varies approximately as the square of the atomic number (Z) of the emitting element (*Moseley's law*). Figure 6.2 shows energy and wavelengths of energetic K, L, and M lines as a function of Z . For most minerals we need only to be concerned with energies up to 10 keV. Also, silicate minerals and glasses are commonly analyzed for the following elements: Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, and Ni (in olivine). Na ($Z = 11$) and Ni ($Z = 28$) cover the atomic numbers of most elements that are commonly analyzed. Figure 6.2 shows that K α lines with maximum energy of less than 10 keV will be exhibited by these elements.

Figure 6.3 shows the energy dispersive spectra of three silicate minerals (olivine, orthoclase, and clinopyroxene) and an oxide mineral. The energies of the lines representing various elements are shown at the bottom of each spectrum. Olivine spectrum shows two strong K α peaks for Si and Mg and a small K α peak for Fe. The relative intensities of these peaks are directly related to the abundance of these elements in the mineral. Actual analysis of this olivine is as follows: 41.93 wt% SiO₂,

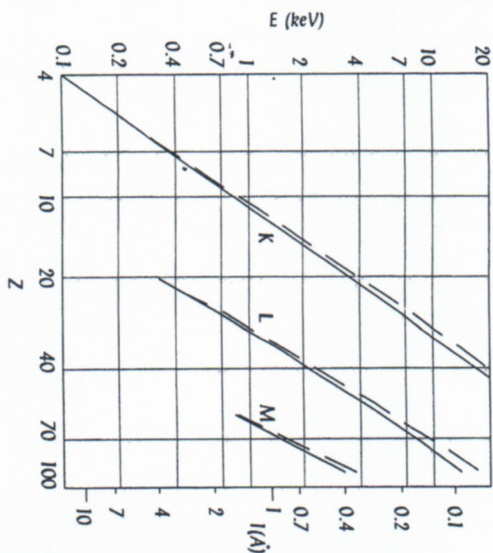


FIGURE 6.2 Energy, wavelength, and atomic number (Z) relationships. Energy (E) and wavelength (λ) of $K\alpha$, $L\alpha$, and $M\alpha$ lines are shown as solid lines and their excitation energies are shown as dashed lines. (From Reed, 1996, *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*, Cambridge University Press)

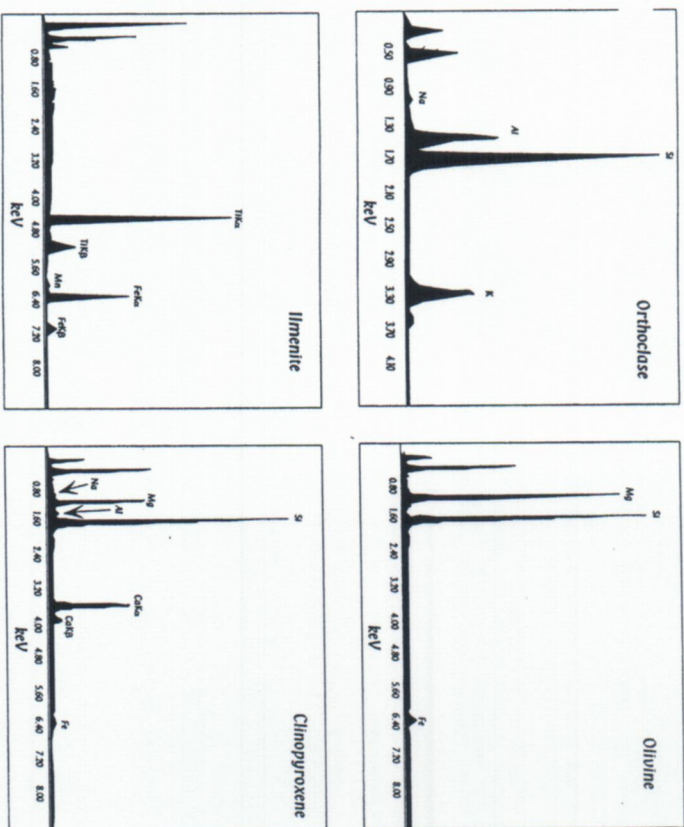


FIGURE 6.3 Energy dispersive spectra of olivine, clinopyroxene, orthoclase, and ilmenite. The energies are marked at the bottom of each spectrum.

49.91% MgO , and 8.16% FeO . In contrast, the clinopyroxene spectrum has additional Na , Al , and Ca peaks. Both $K\alpha$ and $K\beta$ peaks of Ca are visible. Relative to the olivine spectrum, both Fe and Mg peaks are smaller for the clinopyroxene. These peak intensities translate to the following composition of the clinopyroxene: 56.88 wt% SiO_2 , 1.37% Al_2O_3 , 2.26% FeO , 18.96% MgO , 20.09% CaO , and 0.44% Na_2O . Similarly, note the sharper $Al K\alpha$ peak in the orthoclase and the prominent $Ti K\alpha$ and $K\beta$ peaks in the ilmenite sample.

In order to obtain characteristic K lines of various elements, it is clear that E_0 must exceed E_c . It turns out that in order to have the highest probability of K -shell ionization, the E_0/E_c ratio must be about 2.5. It is common practice to use an accelerating voltage of 15 keV in EMP or SEM quantitative analysis of silicate minerals, which produces enough ionizations for useful quantitative analysis of materials.

THE ELECTRON MICROPROBE AND ANALYTICAL SCANNING ELECTRON MICROSCOPE

Basic Instrumentation

The theory and design of the EMP instrument was developed in (1949) by a French graduate student named R. Castaing. Based on this design, the first commercial instrument was built in 1956 by the French instrument maker, CAMECA. CAMECA and many other companies continue to manufacture the SEM and EMP. In both EMP and SEM, high velocity electrons are generated under high vacuum condition from a filament (usually made of tungsten). These electrons are focused through a series of electromagnetic lenses into a very narrow beam. As this beam impacts a target sample, characteristic X-rays and various types of electrons are generated from the sample. These are used to obtain images of the mineral (or any other) sample and to obtain quantitative chemical analysis of it by comparing the X-ray signals against a standard of known composition. Sample preparation is a major endeavor in EMP analysis. The sample must be well polished and be coated with carbon of a certain thickness.

The basic designs of EMP and SEM are similar: they are both high-vacuum instruments and have an electron optical column, a sample chamber, various detectors, and associated instrumentation (e.g., amplifiers) and a computer. The electron optical column has an electron gun, two or more electromagnetic lenses, mechanical apertures, spectrometers and detectors (for wavelength and energy dispersive spectrometry, secondary and back-scattered electron detectors), and a sample chamber (Figure 6.4a,b,c). Figure 6.4a shows a cross section of an electron optical column with the electron gun at the top and the sample at the bottom. Two electromagnetic lenses, a condenser lens above and an objective lens below, are also shown. Although lenses and more complicated designs. Also, EMPs commonly have an optical microscope for sample viewing. The number of electromagnetic lenses and spectrometers varies from instrument to instrument. This figure also shows a schematic wavelength dispersive spectrometer (WDS) in which the characteristic X-rays from a sample are diffracted by a crystal on to the detector. Figure 6.4b shows a schematic representation of an energy dispersive system in which X-rays from the sample are collected by an energy dispersive spectrometer (EDS). An amplifier and a computer process these X-rays and then generates an energy dispersive spectrum of the sample. Figure 6.4c shows a similarly detailed WDS system. An "average" EMP has four wavelength dispersive spectrometers (WDS) and a single energy dispersive spectrometer (EDS).

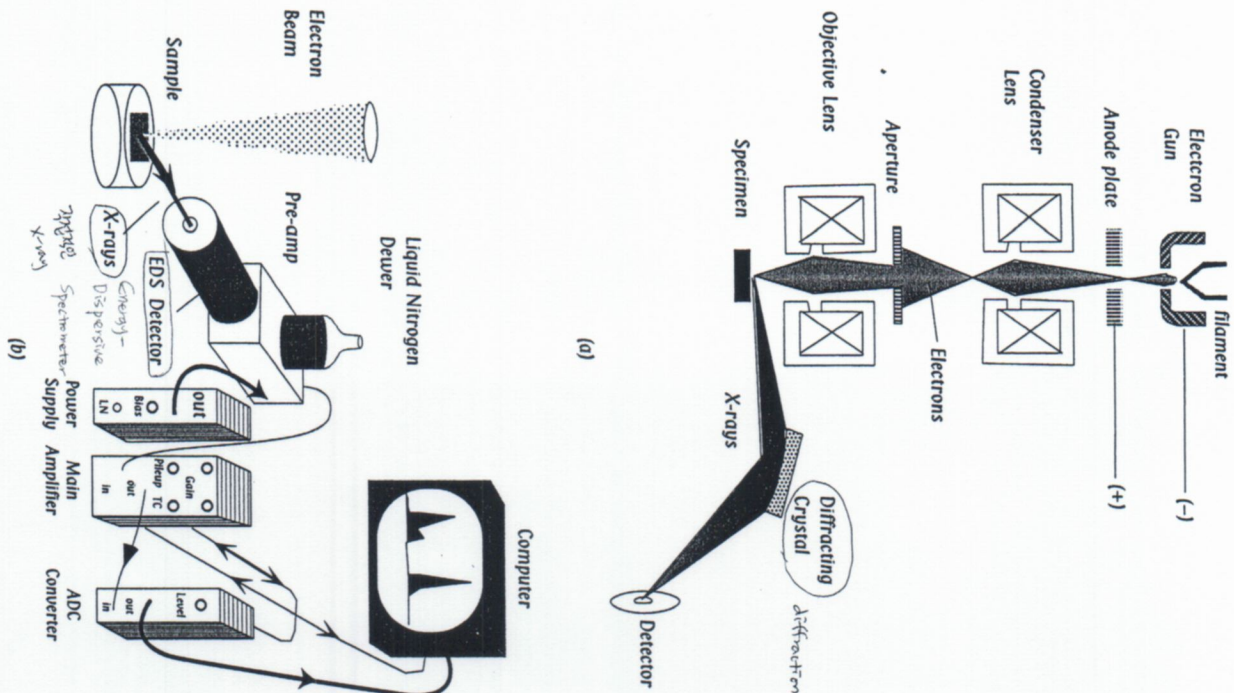


FIGURE 6.4 Schematic diagram showing: (a) the basic elements of an EMP or analytical SEM (EDS detector and scanning coils are not shown), (b) energy-dispersive spectrometer and associated electronics. (Modified from Goldstein et al., 1992, 2nd ed., *Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Publishers)

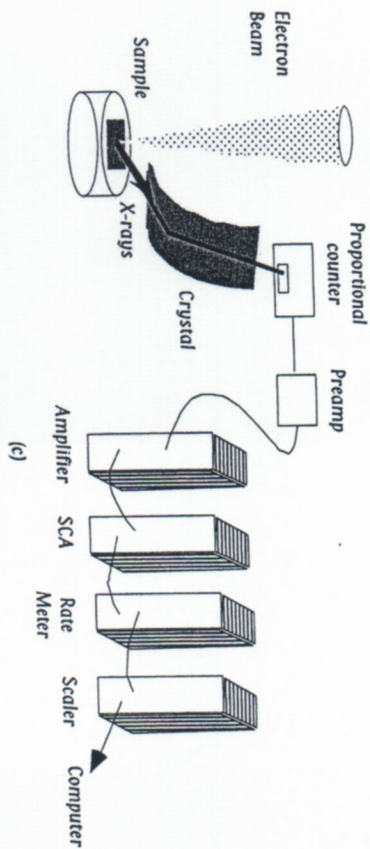


FIGURE 6.4 (continued)

The electron gun (Figure 6.5) houses a filament, which is heated to very high temperatures such that electrons are accelerated out of it. The current passed through the gun is referred to as *accelerating potential*. The filament is housed inside a negatively charged *Wehnelt cylinder*, and a positively charged *anode plate* is located at the base of the electron gun. The basic function of the Wehnelt cylinder and the anode plate is to create a field of equipotentials that force the electrons to form a beam. The *emission current* (the current used to control the emission of electrons from the filament) is the current sent through the anode plate and is generally kept at 100 microamperes for mineral analysis. Several *apertures* are used to focus the beam to a fine spot (1 μm or less in diameter) on the sample. Usually three or more such lenses are used: the lens closest to

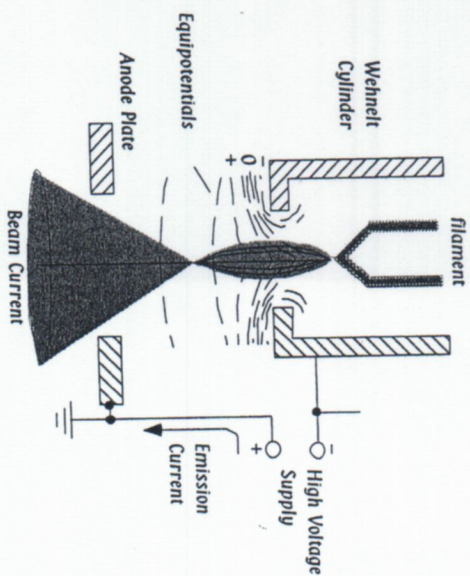


FIGURE 6.5 Electron gun and beam formation. (After Goldstein et al., 1992, 2nd ed., *Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Publishers with permission)

the sample is called an *objective lens*, and the upper lenses are called *condenser lenses*. Electric current flowing through the objective lens may be controlled to obtain a finely focused electron beam on the sample; on the other hand, the condenser lens current can be controlled to obtain a higher or lower beam current. As a matter of first order importance, the finer the focus of the beam the greater the resolution of the image. On the other hand, higher beam current often translates to higher photon counts from a sample and therefore better chemical data in a statistical sense.

BEAM-SAMPLE INTERACTIONS

When a focused electron beam hits the mineral sample (target) with sufficient energy, secondary electrons, backscattered electrons, Auger electrons, cathodoluminescence, fluorescence, and "X-ray continuum" are produced in addition to characteristic X-rays (Figure 6.6a,b,c). In general, mineralogists make use of characteristic X-rays, secondary electrons, and backscattered electrons. *Secondary electrons* are simply target electrons that are let loose by bombarding electrons from the electron beam generated by heating the filament in the electron gun (Figure 6.6b,c). Secondary electrons are generated near the surface of the mineral. Because of their low energies and origin near the surface of the target, secondary electrons are useful in imaging the topography of the mineral surface. *Backscattered electrons (BSE)* are incident beam electrons that are deflected back from inside the sample (Figure 6.6b,c). These come out of the sample with much higher energies than secondary electrons, sometimes reaching the energies of the incident electrons. The energies of BSEs increase with increasing atomic number of the element, and therefore, BSEs can be used to obtain images of zoning and reaction features in crystals. Beam electrons can decelerate as they travel through the coulombic field of adjacent atoms in the sample. Such deceleration results in the emission of X-rays with a wide range of energies that are called *X-ray continuum* or *Bremsstrahlung*. Bremsstrahlung creates a background noise and is therefore more of a nuisance to the analyst who is interested in characteristic X-rays. It affects the minimum concentration level of the element to be determined (i.e., its *detection limit*).

Depending upon E_e and Z of the element, characteristic X-rays may be produced from a substantial, commonly bulbous, volume (called *interaction volume*; Figure 6.7). Figure 6.7 shows two examples of beam-sample interactions in a copper-bearing alloy. The target specimen in Figure 6.7a has a much lower density (and hence lower atomic number or Z) than the one in Figure 6.7b. In both cases the electron beam is of the same diameter, and the sample current and E_e are also the same. We note that the shapes and sizes of the interaction volume in the two examples are very different. The depth of X-ray generation range, R , is much greater in the first case (lower Z). Although not shown here, greater E_e also results in a greater R , all other conditions being equal. Notice that the value of R for copper $L\alpha$ X-rays is greater than that for the $K\alpha$ X-rays in both examples. We conclude that R depends on Z , accelerating voltage (E_e), and the E_e of the X-ray line concerned (Figure 6.7). X-rays are not generated uniformly across the interaction volume. Also, even when all conditions are identical, the ranges for two elements with different Z 's are different; the one with a higher Z will have a smaller range because its E_e is greater. The ranges for $K\alpha$ versus $L\alpha$ X-rays for the same element are different because $L\alpha$ X-rays with lower E_e require less E_e and, therefore, can be generated from greater depth where the E_e is lower than at a shallower depth.

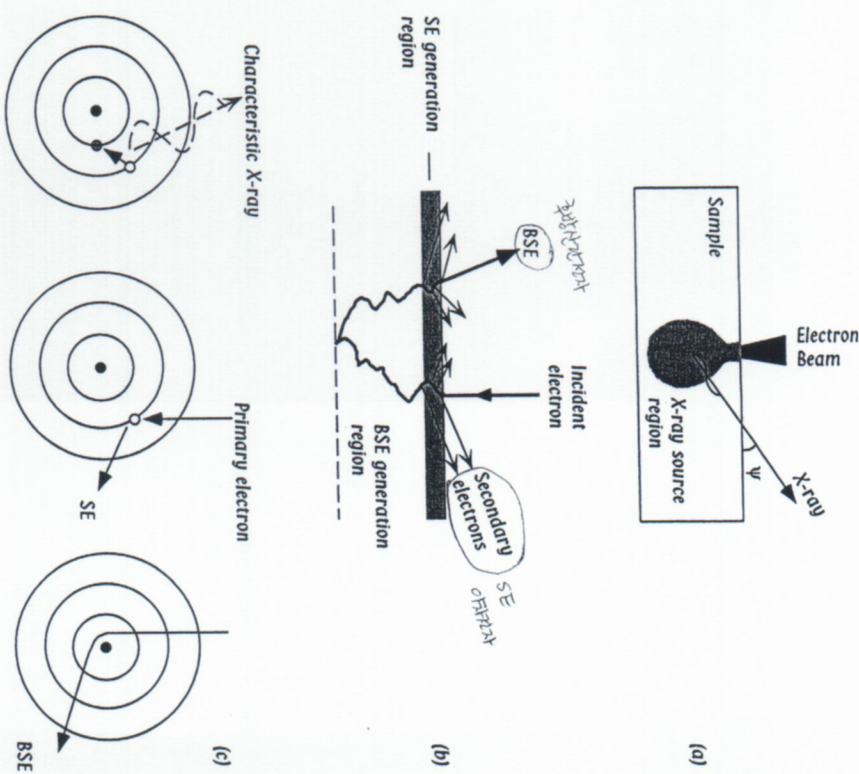


FIGURE 6.6 (a) Interaction volume showing the X-ray generation region and the X-ray take-off angle (ϕ). (b) Generation of backscattered electrons (BSE) and secondary electrons (SE). BSEs are simply the electrons of the incident beam itself that go through the sample and are reflected back with minimal loss of energy. SEs are electrons with weak energies that are knocked off target atoms. (c) The generation of characteristic X-ray by inner shell ionization (left), the generation of secondary electrons (SE) by knocking off a shell electron by an incident (primary) electron (center), and (c) the generation of back-scattered electron (BSE) by scattering back of a beam electron (right).

The range is usually expressed in terms of a parameter called mass-depth (ρz), in which ρ is the density and z (as opposed to Z , which is the atomic number) is the actual depth. The function $\phi(\rho z)$ is used to describe X-ray generation as a function of mass-depth. Note that $\phi(\rho z)$ is not an absolute X-ray intensity (which is very difficult to measure or even calculate) but a normalized intensity (Goldstein et al. 1992). Figure 6.8 shows $\phi(\rho z)$ curves for the $K\alpha$ X-rays for pure copper, titanium, and aluminum. All three curves have the same shape; note that the maximum amount of X-rays are generated somewhat below the surface which is also the region where most of the BSE's come from. The ranges are, however, different (as would be expected; discussed earlier) and the production of X-rays also decreases in a nonlinear

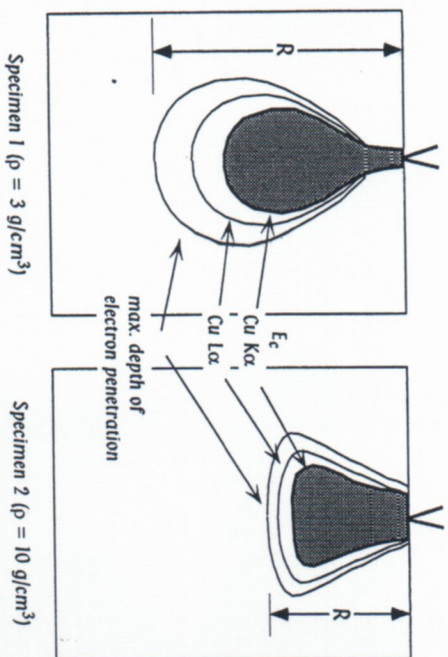


FIGURE 6.7 Range (R) for Cu $K\alpha$ and Cu $L\alpha$ in two different specimens with different densities (left, 3 g/cm^3 and right, 10 g/cm^3). Analytical conditions are the same for both cases. (Redrawn with permission from Goldstein et al., 1992, 2nd ed., *Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Publishers)

fashion in all three cases. Note that $K\alpha$ intensity of Cu ($Z = 29$) is overall less than that for Ti ($Z = 22$) and Al ($Z = 13$). The lesson to be taken from Figure 6.8 is that one should be careful while analyzing fine grained minerals, zoned mineral grains, and mineral grains with fine foreign or exsolved inclusions. Because of the analytical volumes from which different X-rays may be produced during the analysis of a sample, the obtained analysis may include unwanted contributions from such material different overlapping mineral grains at depth within the target sample. Also, not all elements may be affected equally owing to the different ranges of their X-ray lines. Note that in practice, stray signals of "foreign" minerals may be filtered out by evaluating the structural formula of the mineral that is visible on the surface of the sample.

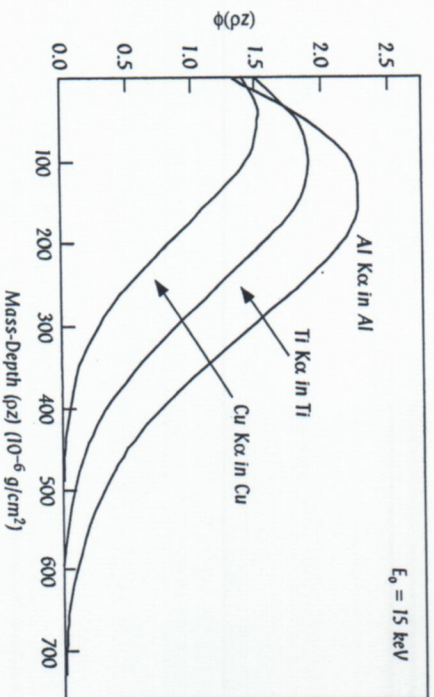


FIGURE 6.8 Calculated $\phi(\rho z)$ curves for $K\alpha$ X-rays for pure Al, Ti and Cu at 15 keV (Redrawn with permission from Goldstein et al., 1992, 2nd ed., *Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Publishers)

ENERGY DISPERSIVE SPECTROMETRY (EDS) AND WAVELENGTH DISPERSIVE SPECTROMETRY (WDS)

X-ray signals are processed by an energy-dispersive and wavelength-dispersive spectrometer. EDS uses a solid-state detector, commonly a lithium-drifted silicon or "Si(Li)" detector, which produces electronic pulses whose heights are proportional to the intensities of the X-ray photon energies. It is a fast method of simultaneously collecting an entire spectrum of energies of photons of different elements. On the other hand, WDS uses Bragg's principle (discussed later) and measures individual characteristic wavelengths of each element, one at a time. While EDS does "parallel" processing of energies of the photons, WDS does a "sequential analysis" since a spectrometer may be "tuned" to only one element's characteristic wavelength at a time. The advantages of EDS are that it allows a fast determination of the proportions of all elements that are present in a mineral and thus is very helpful in a quick identification of the mineral. Quantitative analysis is done better with WDS, especially when it comes to the analysis of elements with $Z < 15$, because the background due to X-ray continuum is higher on the energy spectrum. Also, WDS is sometimes the only way to identify elements whose energy peaks overlap those of another element that is present in greater abundance.

WDS is based on *Bragg's law*, which states that when X-rays of wavelength λ and multiples of λ are "reflected" from identical layers of atoms in a crystal that are separated by a constant distance d (known as *d*-spacing), λ and d are related by the angle of reflection ' θ ' in the following way:

$$n\lambda = 2d \sin \theta$$

where n is 1, 2, 3, ... etc. and reflects the order of reflection (Figure 6.9). In a so-called "fully focusing" WD spectrometer, a crystal of known d -spacing and a detector are placed on the perimeter of an imaginary circle on which the sample surface is also located (Figure 6.10). This imaginary circle is known as the *Rowland circle*. The crystal's inner face is curved to match the curvature of the circle. For different wavelengths of different elements, the Rowland circle must be moved along a linear path such that the take-off angle (ψ), the angle at which X-rays take off the surface of the sample and reach the detector) is held constant. In Figure 6.10 ψ is known for an instrument, L is the distance between the sample and the crystal at any given point, R is the

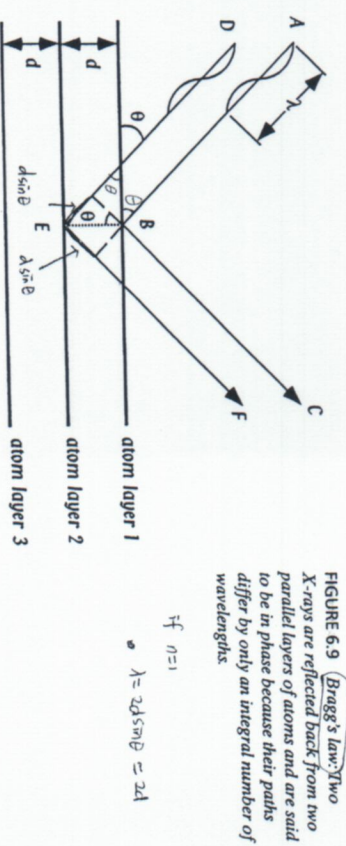


FIGURE 6.9 (Bragg's law): Two X-rays are reflected back from two parallel layers of atoms and are said to be in phase because their paths differ by only an integral number of wavelengths.

$$n\lambda = 2d \sin \theta$$

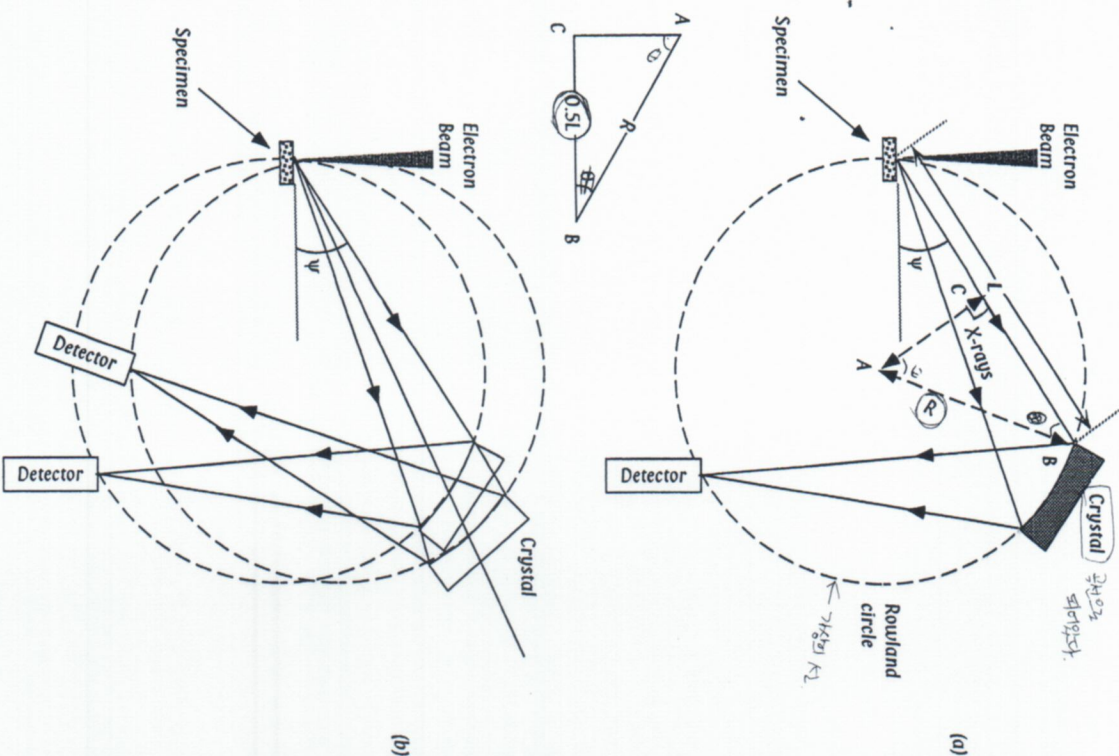


FIGURE 6.10 Schematic drawings showing how wavelength-dispersive spectrometry works: (a) The electron beam hits the sample and generates characteristic X-rays, which are reflected by a curved crystal toward the detector, where each photon is received and passed through an amplifier and other processing units. The radius of curvature of the crystal, the centroid of the sample, and the detector all lie on the perimeter of an imaginary circle, known as the Rowland circle. θ is the diffraction angle; ψ is the take-off angle. The triangle ABC (inset) shows the relationship between R , L , and θ which is utilized in the WDS method (see text). (b) In a fully focusing spectrometer, the positions of the detector and the crystal are moved for different X-ray lines, although the take-off angle remains constant. (Modified from Goldstein et al., 1992, 2nd ed., *Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Publishers)

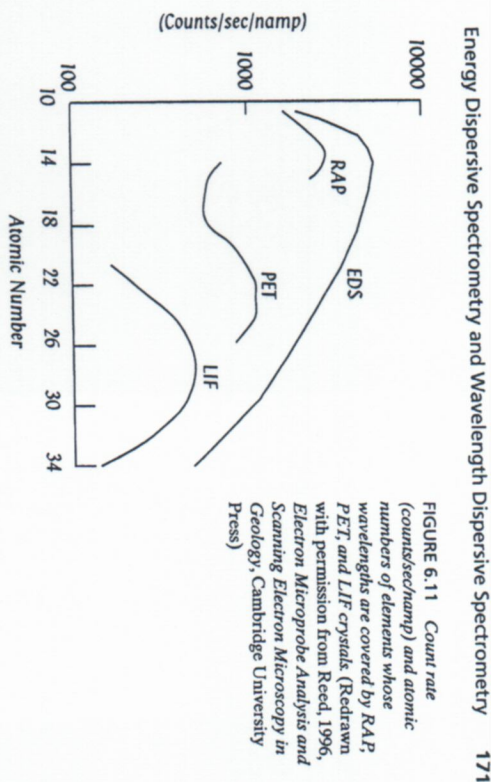


FIGURE 6.11 Count rate (counts/sec/namp) and atomic numbers of elements whose wavelengths are covered by RAP, PET, and LIF crystals. (Redrawn with permission from Reed, 1996, *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*, Cambridge University Press)

radius of the Rowland circle, and θ is the Bragg angle. From the triangle ABC in Figure 6.10, $\sin \theta = L/2R$. Transferring this value of $\sin \theta$ to Bragg's law ($n\lambda = 2d \sin \theta$) we obtain the following:

$$n\lambda = dL/R$$

$$\frac{n\lambda}{dL} = \frac{1}{R}$$

The above relationship forms the basis of the functioning of WDS spectrometers. Because d -spacing of the crystal is an important factor in resolving wavelengths of X-rays of different elements, several different crystals with different d -spacing and different wavelength coverage (Figure 6.11) are needed to analyze most elements in a mineral. This is done with the use of four or more spectrometers, each fitted with one crystal. More commonly, each spectrometer contains two crystals that can be flipped one at a time into the path of X-rays. Geologists commonly use ADP (or PET), LIF, and RAP (or TAP) crystals. Each of these can detect different wavelengths of different elements (Table 6.1). Table 6.1 lists the most commonly analyzed elements by their atomic numbers, $K\alpha$ or $L\alpha$ lines, their intensities, and peak positions on four of the more commonly used WDS crystals—LIF (Lithium Fluoride), ADP (Ammonium dihydrogen phosphate), RAP (Rubidium acid phthalate; try pronouncing this name), and PET (Pentaerythritol). The modern WDS spectrometers are commonly equipped with a greater variety of analyzing crystals that increase peak intensity of some of the more difficult elements. The analyst may a combination of crystals in different spectrometers to analyze a whole range of elements in a mineral; for example, let us consider the analysis of a clinopyroxene. The routinely analyzed oxides in a clinopyroxene are SiO_2 , TiO_2 , Al_2O_3 , Cr_2O_3 , FeO (* represents all Fe assumed to be ferrous and analyzed as such), MnO , MgO , CaO , Na_2O . Based on Table 6.1 one may choose the following set up for analysis.

Spectrometer#	Crystal	Elements for Analysis
1	RAP	Na, Mg
2	ADP (or PET)	Al, Si, Ca
3	LIF	Cr, Ti, Mn, Fe

TABLE 6.1 Atomic number and peak positions of elements of geological interest.

El	Line	Z	I	LIF	RAP	ADP	PET
Na	K α	11	100		1.8360		
Mg	K α	12	100		1.5246		
Al	K α	13	150		1.2856		
Si	K α	14	150			3.1562	3.8415
P	K α	15	150			2.6969	3.2824
S	K α	16	150			2.3304	2.8364
K	K α	19	150			2.0334	2.4749
Ca	K α	20	150			1.4163	1.7238
Ca	K α	20	150	3.35948		1.2714	1.5474
Ti	K α	22	150	2.74973			1.2665
Cr	K α	24	150	2.2910			
Cr	K α	24	100		3.3358		
Min	K α	25	150	2.10314			
Min	K α	25	100		2.9983		
Fe	K α	26	150	1.93735			
Fe	K α	26	100		2.7115		
Ni	K α	28	150	1.65919			
Ni	K α	28	100		2.2446		
Cu	K α	29	150	1.54184			
Cu	K α	29	100		2.0558		

The actual choice of crystals and spectrometers is dependent on many factors, such as the peak position relative to the limits of the spectrometer motion, peak overlap problems, counting statistics, etc. It is beyond the scope of this book to discuss these factors in any detail.

QUANTITATIVE ANALYSIS

The basic concept of quantitative analysis of minerals (or any solid material) is based on the fact that the intensities of X-rays for different elements are proportional to their concentrations in the sample. The concentration of an element in an unknown sample may be determined from its X-ray intensity if the X-ray intensity versus composition relationship is obtainable from a known standard whose composition had been determined by other methods (wet chemistry, for example). If $[I_i]^u$ and $[C_i]^u$ are X-ray intensity and composition, respectively, for an element 'i' in an unknown sample 'u', and $[I_i]^s$ and $[C_i]^s$ are those of the same element in the standard 's', then:

$$\left(\frac{[C_i]^u}{[C_i]^s} \right)^r = \left(\frac{[I_i]^u}{[I_i]^s} \right)^r \quad (6.1)$$

The term on the right hand side is conventionally known as the *k-ratio*. The concentration of an unknown element with a $Z > 16$ determined from the above equation is generally in error by about 10%; and for light elements it can be much worse. Figure 6.12 demonstrates the effect of matrix on chemical analysis in a series of Fe-Ni alloys between pure Fe and pure Ni compositions. The lines marked "ideal" show a one-to-one correspondence of the *k-ratio* and concentration. The "measured" curves reflect the actual concentrations as determined from intensity ratios measured on the EMP. Note that the intensities of Ni X-rays are always too high whereas those of

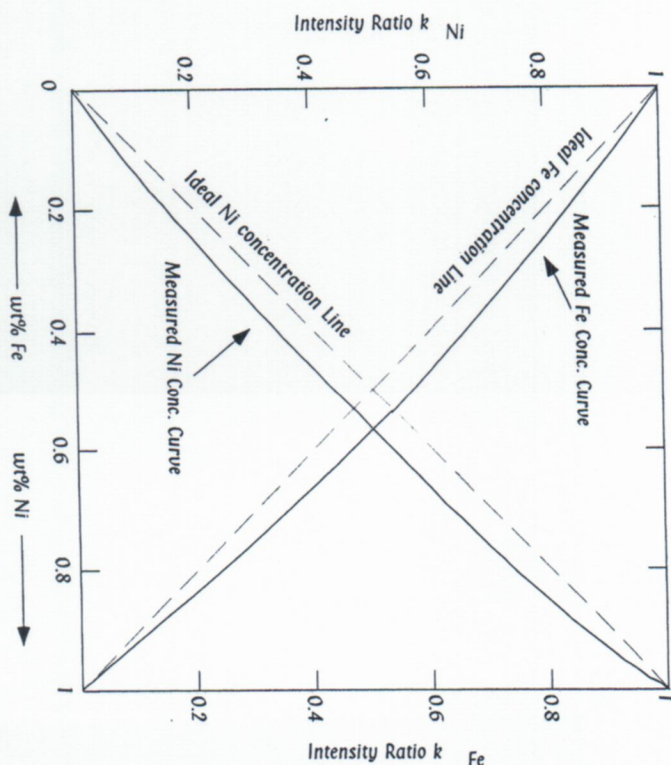


FIGURE 6.12 Actual concentrations ("ideal") of Ni and Fe in a series of Ni-Fe alloys from $Ni_{100}Fe_0$ to $Ni_{00}Fe_{100}$ are compared with measured concentrations as determined from intensity ratios of Ni and Fe. (Redrawn with permission from Goldstein et al., 1992, 2nd ed., *Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Publishers)

Fe are always too low relative to their ideal values. This is because the Fe K α line has a lower E_c than the Ni K α line and therefore contributes extra photons from a region that is below the range for Ni. The opposite is true for the Fe K α line. This difference is due to errors contributed by the presence of other elements in the same sample, and is due to errors contributed by the presence of other elements in the same sample, and some nominal correction must be made to the raw intensity data. These corrections are known as *matrix correction factors*, and they stem mainly from three things: atomic number (Z), X-ray absorption (A) and fluorescence (F). Detailed discussion of these factors is beyond the scope of this book and may be found in the reference listed. A simple way to express the concentration and intensity ratios and matrix correction factors is as follows:

$$\left(\frac{[C_i]^u}{[C_i]^s} \right)^r = \left(\frac{[I_i]^u}{[I_i]^s} \right)^r \times [ZAF]_i, \text{ where } ZAF \text{ is the correction factor for the same element.}$$

These correction factors depend to a significant degree on the beam current, nature of the sample, and the take-off angle (ψ) of the instrument. ψ is the angle contended between the mineral surface and the detector. For example, the smaller the take-off angle, the more sample X-rays will have to travel through and therefore, more absorption corrections will need to be made. The take-off angle of modern EMP's is fixed at 40° .

All modern instruments come with matrix correction software that allows three different options for matrix corrections—ZAF, $\phi(\rho z)$, and Bence-Albee corrections. The first two are based on metal alloys made in the laboratory, and the third

is based on pure oxides synthesized in the laboratory. Most geologists have found the Bence-Albee corrections to be most useful for mineral analysis because, in geological samples, errors resulting from the fluorescence factor are small. Note that matrix corrections would be minimal if the standard were chosen to be chemically and structurally close to the unknown; that is, if a diopside clinopyroxene is used to analyze another similar pyroxene in the unknown sample, the corrections would be few, if any. Mineral standards are often hard to come by, however, when they are available, one should use them for most of the major elements present. According to Goldstein et al. (1992), $\phi(\rho z)$ correction method is superior to the other two methods and does not require the use of a whole range of standards, as is the case for the Bence-Albee method.

EMP AND SEM ANALYTICAL CONDITIONS

Geological samples are mainly silicates and are poor conductors. Therefore, they need to be coated with a conducting material, and carbon is usually the conducting material of choice. The quality of the analysis of minerals and glasses depends upon many factors, perhaps the most important of which are accelerating potential, counting statistics, standards, nature of the material being analyzed, and instrument drift (see Goldstein et al. 1992 for a detailed discussion of these factors). For geological samples, the accelerating potential is commonly set at 15 or 20 kV. However, for high resolution imaging purposes, one may use a voltage of 25–30 kV. Such higher accelerating potential is also needed when the goal is to analyze elements of high atomic number (e.g., Uranium). The number of photon counts per second that may be obtained for a particular element depends on the abundance of the element in the mineral, the beam current and sample current, and the detector (and associated electronics). An optimum set of numbers for routine silicate mineral/glass analysis are as follows: accelerating potential, 15 kV; emission current, 100 microamps; sample current, 30 nanoamps. A minimum of 10,000 total counts is necessary for most major elements.

The nature of the target sample is an important factor in the analysis: the greater the concentration of "volatile" elements (i.e., elements with atomic number of <12, such as Na), the greater the risk of a problem due to volatile loss during analysis. This problem is generally manifested in low oxide totals, and can be minimized by using low sample current, a defocused beam (diameter $\sim 10 \mu\text{m}$), or a shorter counting time.

The electron beam may "drift" considerably (i.e., the beam current may fluctuate) during the course of an analysis. Such drift is common in old instruments and may result in problematic analysis. In order to check for such problems, it is important to analyze a known standard every 3–4 hours during the course of analysis.

The quality of the crystal used in a detector and associated electronics can pose a problem for old microprobes but is usually not a factor for new SEMs or EMPs. Over the years these crystals become bad, and when this happens the count rate goes down sharply, at which point they must be replaced.

The "goodness" of a mineral analysis is checked by analyzing a standard of similar composition, the oxide totals, and the structural formula (see Box 6.1). When dealing with minerals or glasses containing structural (OH) or (CO₃)²⁻, it is not possible to use the oxide totals criterion above. For hydrous minerals, often with structural vacancies, it may be hard to use the structural formula as well. At any rate, for most geological purposes, the analysis of hydrous or carbonate minerals is generally acceptable.

6.1 CHEMICAL ANALYSIS OF MINERALS

The quality of chemical analysis of materials is generally excellent with the electron microprobe or the analytical scanning electron microscope. However, the analyses are not always good, and the analyst must know how to separate the good from the poor analyses. One way to do this is to check the *structural formula*, which is simply the proportion of cations relative to a fixed number of oxygens in the mineral's formula.

Let us consider the structural formula calculation of the mineral clinopyroxene, which has six oxygens and four cations in its formula. For example, diopside (CaMgSi₂O₆) has six oxygens and four cations (Ca²⁺ + Mg²⁺ + Si⁴⁺). Furthermore, clinopyroxene has primarily two types of cation sites—tetrahedral (or T site) and octahedral (M site; Chapter 5). Ideally, in a real pyroxene composed of 9 or 10 major and minor elements, the total number of cations of Si⁴⁺ and Al³⁺ filling up its tetrahedral site (or T site) should be two, and the rest of the cations should then add up to two—filling up the M1 and M2 cation sites in pyroxene's atomic structure.

(See Chapter 5.) In general, a pyroxene analysis is acceptable if the total cations add up to any value between 3.98 and 4.02. However, some authors may impose more stringent acceptability "filters."

The sample calculation shown in Table Bx 6.1 is an actual EMP analysis on a clinopyroxene in a Hawaiian xenolith, which shows that the analysis is good, based on the above mentioned criterion, because the total number of cations per 6 oxygens is 3.997. Similarly, one may use "total cation filters" for olivine (cation sum per 4 oxygens = 2.98–3.01) and feldspars (cation sum per 8 oxygens = 4.98–5.02). However, because EMP analysis cannot distinguish between the valence states of an element, the calculation of structural formula may become a tricky issue for minerals like spinel, garnet, and amphibole, which can contain a significant amount of Fe³⁺, in addition to Fe²⁺. Hydrous or other volatile-bearing mineral formula calculation is further complicated by the presence of elements that are not normally analyzed for.

TABLE Bx 6.1 Mineral structural formula calculation.

Oxide	A	B	C	D	E	F	G	H	I	J
	Cations in Oxide						Real Oxygens per Cation			
	Moles						Real Oxygens			
	Cations						Normalized to 6 Oxygens			
	Cations						Cations			
	Moles						Cations			
	Moles						Cations			
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X-RAY POWDER DIFFRACTOMETER (XRD)

The utility of X-rays in determining crystal structure is well known. This is one area of study where 14 Nobel prizes in Physics have been awarded (Battey and Pring 1997). Sophisticated single crystal structure determination requires different types of X-ray diffractometers, which cannot be discussed here. Instead, we will briefly discuss the most commonly used X-ray machine, an X-ray powder diffractometer, for routine mineral identification work.

The guiding principle on which an XRD operates is Bragg's law. In X-ray powder diffractometers, the source of X-rays is an evacuated X-ray tube (Figure 6.13), in which a beam of electrons is generated from a tungsten filament by applying an accelerating voltage of 20–100 kV. These electrons hit a metal target (usually copper for geological samples) and produce X-rays. These X-rays then collide with a target sample and get diffracted and collected by a detector. The signals received by the detector are then passed on to a computer, which identifies the 'reflections' and their peak intensities with reference to the angle 2θ and identifies the sample.

The procedure is simple: a mineral (or rock) is powdered to fine size and thinly and evenly spread, along with a bonding agent (acetone is commonly used), on a glass slide. This glass slide is then clamped onto a stage. The X-ray beam and the sample are lined up along a straight path. The detector sits on the other side of the sample from the X-ray source and moves along a circular arc (Figure 6.14) in order to catch the X-ray photons diffracted over a 2θ value of 2–60° (for most routine work).

The basic idea is that although the powdered sample will contain mineral grains of all kinds of orientation, reflections from a particular set of (hkl) planes of many different grains will obey Bragg's law. These may be matched with diffraction patterns of known minerals, and the unknown mineral may thus be identified. Most instruments can routinely identify minerals with automated systems that are attached to the actual instrument.

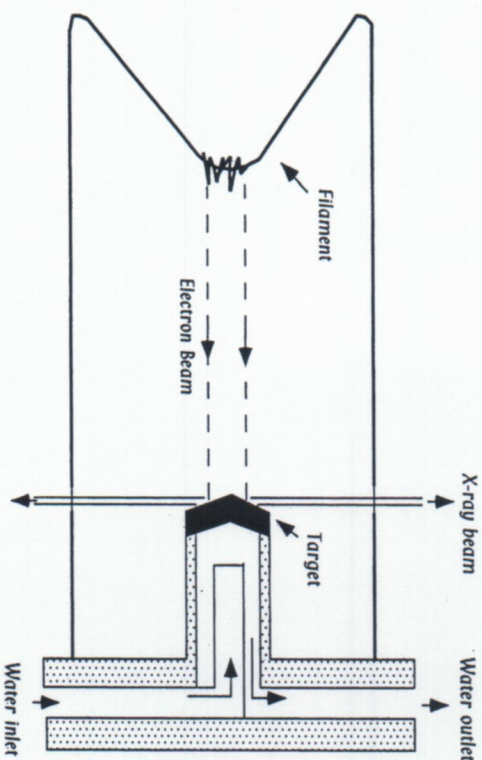


FIGURE 6.13 Schematic drawing of an X-ray tube. (Redrawn from Battey and Pring, 1997, 3rd ed., *Mineralogy for Students*, Addison Wesley Longman)

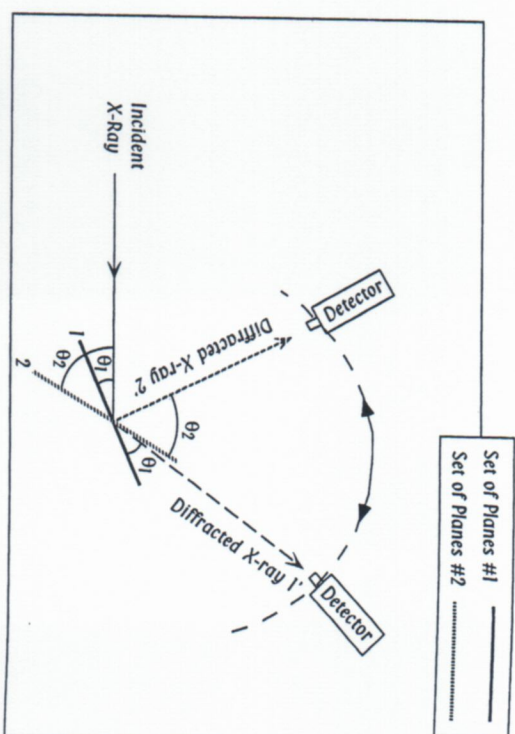


FIGURE 6.14 The principle of X-ray powder diffraction. The X-ray beam diffracted by a particular plane of atoms in a crystal is detected by a detector, which revolves around the sample in such a way that it can detect X-rays coming off the sample at many different angles.

SUMMARY

- [1] Three instruments that are commonly used in mineralogical laboratories are the scanning electron microscope (SEM), the electron microprobe (EMP), and the X-ray powder diffractometer (XRD). SEM and EMP are used for imaging and chemical analysis of minerals, whereas XRD is used to identify crystalline phases, particularly fine-grained ones.
- [2] In all three instruments, a high-energy electron beam is used to generate X-rays from a target. In the case of SEM and EMP, the target is the sample to be analyzed; but in XRD, the target is simply the source of the X-rays used to hit a sample and investigate its crystalline structure.
- [3] Two types of analytical procedures are used in SEM and EMP: wavelength and energy dispersive spectrometry, or WDS and EDS. WDS and XRD methods are based on Bragg's law. WDS analysis is highly quantitative, whereas EDS analysis can be semi-quantitative to qualitative.

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