12 X-ray Diffraction and Mineral Analysis

KEY CONCEPTS

- X-radiation, discovered in 1895, was the key to understanding atomic arrangements in crystals.
- X-rays may have many different wavelengths but for diffraction studies we isolate one.
When X-rays interact with atoms, the rays are scattered in all directions; coherent scattering by multiple atoms produces X-ray diffraction.

Directions of diffraction tell us the spacings between planes of atoms in a crystal; intensities of diffraction tell us the number of atoms on those planes.

We use a powdered sample for routine mineral identification.

Compositional variations cause slight variations in X-ray patterns.

Single crystal diffraction data allow crystallographers to figure out where atoms are in a unit cell.

Scanning electron microscopes allow high-magnification imaging of mineral crystals and of thin sections.

Electron microprobe data yield mineral compositions based on X-ray intensities.

Other important analytical techniques include X-ray fluorescence, atomic absorption, inductively coupled plasma mass spectrometry, ion microprobe, Mössbauer spectroscopy, visible and infrared spectroscopy, and Raman spectroscopy.

12.1 X-ray Diffraction

12.1.1 The Discovery of X-rays and Diffraction

Scientists studied minerals for hundreds of years before the discovery of X-rays. By the late nineteenth century, mineralogists knew that crystals had ordered and repetitive crystal structures. They hypothesized about atomic arrangements and the nature of crystal structures, but they lacked direct evidence. Some ideas about crystal structure were generally accepted, while others were poorly understood and hotly debated. Without a way to test hypotheses, development of an understanding of atomic arrangement and of
bonding in crystals was stalled.

12.2 Röntgen at work in 1896

Wilhelm Conrad Röntgen’s discovery of X-rays in 1895 allowed mineralogists to proceed with their studies and eventually led to a greater understanding of crystal structures. Mineralogists quickly discarded many hypotheses disproved by X-ray studies; just as quickly, they developed and tested new ones. In less than two decades, scientists developed a firm theoretical basis for understanding how atoms are arranged in minerals.

Today we accept without question the idea that atoms bond together in regular arrangements to make crystals. We draw pictures, make enlarged models, and study the details of crystal structures of thousands of minerals. All this knowledge would have been unobtainable if Röntgen and his coworkers had not recognized the importance of some curious phenomena they observed while studying cathode ray tubes (early versions of television tubes) in 1895.

Röntgen taught and studied physics at the University of Würzburg in Germany. He was studying the relationship between matter and force as charged particles flowed from a heated
filament in an evacuated glass tube. By chance, he observed that a nearby piece of barium platinocyanide fluoresced when he turned on the tube. Röntgen deduced that electrons interacting with the walls of the tube produced a high-energy form of radiation, and he showed that the radiation could penetrate paper and even thin metals. Because the radiation seemed to behave differently from light, he thought it a completely different phenomenon, calling it \textit{X-radiation}. Various physicists searched for an understanding of the nature of \textit{X}-radiation. X-rays became inextricably involved with mineralogy when Max von Laue successfully used crystals as a tool in this search.

12.3 Diffraction

Gratings containing fine slits disperse light into different colors

The diffraction of light was well understood at the time. Physicists routinely measured the wavelengths of colored light using finely spaced \textit{diffraction gratings}. The gratings consist of many parallel slits (or sometimes grooves), typically spaced between 0.0002 and 0.03 mm apart. Light passing through a grating is \textit{dispersed} – which means it is separated into different colors that go in different directions (Figure 12.3).

In 1911, von Laue, a physics professor in Münich, determined that lines in diffraction gratings were not spaced closely enough to diffract X-rays. This partly explained Röntgen’s
confusion about the relationship between light and X-rays. Von Laue hypothesized that the distance between atoms in crystals, being much less than the distance between lines in diffraction gratings, could lead to X-ray diffraction. And, so he ushered in the field of X-ray crystallography.

In 1912, Walter Friedrich and Paul Knipping confirmed von Laue’s ideas when they caused X-rays to pass through crystals of copper sulfate (CuSO₄) and sphalerite (ZnS) and recorded diffraction patterns on film (Figure 12.4). Their studies showed that X-rays are electromagnetic waves similar to light, but with much shorter wavelengths. They also confirmed that crystals must have a regular crystal structure.

The impact of the work by von Laue and his students was immense. Paul Debye and Paul Scherrer soon improved X-ray techniques. They showed that all crystals have a lattice and that lattices vary in their symmetry. In 1913 William H. Bragg and his son William L. Bragg determined the arrangement of atoms in sphalerite, ZnS, using data obtained with X-ray studies. For the first time, mineralogists knew the actual locations of atoms within a crystal. Similar studies on other crystalline compounds soon followed as Linus Pauling and other
scientists realized the power of X-ray diffraction.

Early X-ray studies were tedious. Scientists could spend an entire career determining the atomic arrangement in only a few minerals. Today, with sophisticated equipment and high-speed computers, crystal structure analyses are often routine and can be completed in less than a day. It is important to remember, however, that without the pioneering work of Röntgen, von Laue, the Braggs, Pauling, and others, we would have no detailed knowledge of how atoms are arranged in minerals. In 1901 Röntgen received the first Nobel Prize for Physics; von Laue received the same prize in 1914, and both Braggs were the recipients in 1915.

12.1.2 What are X-rays?

X-rays are a form of electromagnetic radiation (Figure 12.5). Whereas the wavelengths of visible light are $10^{-7}$ to $10^{-6}$
meters, X-ray wavelengths are only $10^{-11}$ to $10^{-8}$ meters. Long-wavelength X-rays grade into ultraviolet light; shorter wavelengths grade into cosmic and gamma rays. Mineralogists usually give X-ray wavelengths in angstroms (1Å equals $10^{-10}$ meters). The copper radiation commonly used in X-ray studies has $\lambda = 1.5418$Å.

The frequency ($\nu$) and wavelength ($\lambda$) of electromagnetic radiation are inversely related. Planck's law relates them to energy:

$$E = h\nu = hc/\lambda$$

In this equation $h$ is Planck's constant and $c$ is the speed of light in a vacuum. Because of their short wavelengths and high frequencies, X-rays have high energy compared with visible light and most other forms of electromagnetic radiation. High energy allows X-rays to penetrate many natural materials, as observed by Röntgen in 1895.

X-rays of highest energy, called hard radiation, are used in many manufacturing and industrial applications, such as checking steel for flaws. X-rays of relatively low energy, called soft radiation, are used by mineralogists and for medical diagnoses. Soft radiation is the most dangerous to people because, rather than passing through tissue like many hard X-rays and gamma rays, soft X-rays interact with atoms in cells and tissues, causing damage. Because of the potential health hazards, crystallographers take special care to avoid exposure to the X-rays in their experiments.
Mineralogists use X-ray tubes (Figure 12.6) to generate X-rays for diffraction studies. In the tubes, a heated filament releases a beam of high-velocity electrons that strike a metal target. Some of the high-velocity electrons that hit the target cause emission of a continuous spectrum of X-rays called *continuous radiation* or *white radiation* (the “whale-shaped” hump in Figure 12.7).

Other electrons collide with electrons orbiting atomic nuclei in the target material and bump the electrons temporarily into a high energy level. As the target electrons return to lower energy levels, they emit energy as X-rays. The energy difference between the two levels is proportional to the energy and frequency, and inversely proportional to the wavelength, of X-rays emitted. Because some electrons are elevated to higher levels than others, and because they do not all return to the same levels, typical X-ray tubes emit *characteristic radiation* (the peaks in Figure 12.7) having several different wavelengths. The wavelengths of the characteristic radiation depend on the metal in the target of the X-ray tube. So, X-ray tubes emit *polychromatic* radiation, radiation having a range of wavelengths, but most of the energy is channeled at specific wavelengths. We designate the different characteristic X-ray wavelengths using combinations of English (*K, L, M*) and Greek (*α, β, γ*) letters. The most intense peak is designated *Kα* (Figure 12.7).
The most common X-ray tubes have a copper target. Copper has more than one characteristic X-ray wavelength, but interpretation of diffraction results is easiest if we use one (monochromatic radiation). So we use copper’s most intense radiation, \( K\alpha \), for most routine X-ray studies. To isolate \( K\alpha \) radiation from the other wavelengths, X-ray machines have filters, monochromators, or solid-state monochromatic detectors. X-ray tubes emit two nearly equal wavelengths of Cu \( K\alpha \) radiation: the wavelength of \( K\alpha_1 \) is 1.5401Å and the wavelength of \( K\alpha_2 \) is 1.5443Å. They are so similar that, although two wavelengths are present, for most applications the radiation is effectively monochromatic, and we take a weighted average of \( K\alpha_1 \) and \( K\alpha_2 \). We assume a \( \lambda \) value of 1.5418Å.

**12.1.3 Interactions of X-Rays and Atoms**

When an X-ray strikes an atom, the wavelike character of the X-ray causes electrons, protons, and neutrons to vibrate. Heavy protons and neutrons vibrate less than much lighter electrons. The oscillating electrons reemit radiation, called secondary radiation, at almost the same frequencies and wavelengths as the incoming beam. This creates X-ray wavefronts (dashed lines in Figure 12.8) that travel in all directions from the atom, much the same way that circular
ripples disperse in water (Figure 12.8b). The difference in radius of adjacent wavefronts is the wavelength, \( \lambda \). This process, called **scattering**, is not the same for all elements, nor is it the same in all directions.

Because heavy elements have atoms with more electrons, they scatter more efficiently than light elements, and scattering by heavy elements can completely mask scattering by light ones. As a result, X-ray crystallographers often have trouble measuring the effects of light atoms, such as hydrogen, when X-rays interact with crystal structures. As X-rays scatter in different directions, they interact with electron clouds in various ways. Overall, those scattered at high angles to the incident beam are less intense than those scattered at low angles.

Besides being scattered, when X-rays interact with atoms in a crystal, some electrons temporarily bump up to higher energy states. As the electrons return to their normal state, a release of radiation characteristic of the element comprising the target atom (in the crystal) occurs. This process, called **X-ray fluorescence (XRF)**, is similar to the interaction of electrons and atoms in the target metal of an X-ray tube, but results from interaction of X-rays and atoms in the crystal. X-ray fluorescence, while not widely used by mineralogists, is the basis for a common analytical method used by petrologists and geochemists.

**12.1.4 Interference of X-Ray Waves**
12.9 Wave interference

Just like visible light, X-rays propagate in all directions and may interact, or interfere, with each other (Figure 12.9). Two parallel X-rays of the same wavelength can exhibit constructive interference or destructive interference. If constructive, it means that the waves are in phase – that their wave peaks coincide. In such a case, wave energies add, increasing X-ray amplitude. Destructive interference occurs when waves are out of phase – one is moving up while the other is moving down. When destructive interference occurs, waves can appear to cancel. Often, waves are partially in phase and partially out of phase.
12.10 Interference of waves from two atoms

Figure 12.10 shows two atoms emitting monochromatic X-radiation. The solid lines show wavefronts moving away from each atom. If we could move an X-ray detector around the atoms, we would find that energy is intense in some directions (where wave peaks coincide and waves interact constructively). In other directions, the detector would register no X-rays due to destructive interference. This channeling of energy in specific directions is diffraction. The directions of diffraction depend on X-ray wavelength and distance between the two X-ray sources.

A narrow slit, a series of parallel grooves in a diffraction grating, regularly spaced atoms in a crystal, and many other things can cause diffraction. The main requirement is that two or more sources emit, or scatter, monochromatic waves.

In principle, all electromagnetic radiation can be diffracted, but unless the spacing of atoms, slits, or gratings is similar
to the wavelength of the radiation, diffraction will not occur. Fortunately for mineralogists, atoms have radii on the order of angstroms. Because atoms pack closely together in crystals, space between atoms is of the same magnitude. So, atomic radii and spacing are about the same dimension as the wavelength of X-rays. Consequently, X-rays interacting with atoms in crystals can lead to intense X-ray diffraction. This is the understanding that led von Laue and his coworkers to their successful experiments.

12.1.5 Diffraction by a Row of Atoms

To discuss diffraction by a row of atoms, we can use the analogy of a group of campers standing on a lake dock. One camper throws a rock in the water, producing wave fronts that spread out in concentric circles before eventually dying out (Figure 12.11a).
Next, five campers on the dock all drop rocks into the water at different times, making many circular wavefronts. The wavefronts work with each other constructively in some directions and destructively in others. Most are out-of-phase and the waves disappear quickly.

But then they try an experiment. Five campers stand on the dock and all drop a rock into the water simultaneously. Each rock produces a circular wavefront. The five circular wavefronts are in phase and together create a straight wavefront that moves across the lake before eventually losing energy (Figure 12.11b). The rocks produce waves similar to a parallel set of wind-driven waves that might move across the ocean or across a lake (Figure 12.11c). If you are in a boat and see the waves coming toward you, you cannot tell that they were created by multiple in-phase point sources.

When a row of atoms scatters an X-ray beam, the atoms can produce a coherent wavefront similar to the one produced when rocks hit water simultaneously. Figure 12.11b could be showing a row of atoms each emitting X-ray waves with identical wavelengths. If all the atoms emit a wave simultaneously, the waves will create a straight wavefront moving away from the row. This is what happens when an incident X-ray beam strikes a row of atoms. The atoms scatter X-rays and create coherent wave fronts even if the incident wave hits the row of atoms at an angle. So, constructive interference produces a wavefront moving perpendicularly away from the row of atoms. And, as we will see shortly, wavefronts also travel in other directions.
Figure 12.12a shows circular wavefronts emitted by atoms in a row. The difference in radius of adjacent wavefronts is the wavelength, $\lambda$. As described above, the waves, which have all traveled the same distance, combine to form straight wavefronts moving perpendicular to the row.

But because one cycle of a wave is the same as any other, it does not matter if waves have traveled different distances. If their peaks correspond, they are in phase. So, Figures 12.12b, c, and d show that coherent wavefronts also move in other directions. In Figure 12.12b, waves emitted by adjacent atoms differ in travel distances by $1\lambda$; in Figure 12.12c by $2\lambda$; and in Figure 12.12d by $3\lambda$.

Thus, we see that diffraction by a row of atoms in 2D produces wave fronts traveling in many directions. This is the same when 3D crystals diffract X-rays – diffracted rays go in many directions in 3D space.
12.13 Incident and diffracted wave fronts

The geometry in Figure 12.12 yields a simple relationship between wavelength ($\lambda$), atomic spacing ($d$), and the angle of diffraction ($\alpha$). In Figure 12.13, diffracted waves travel different distances; each wave is behind (or ahead of) the one next to it by some integer number of wavelengths ($n\lambda$). If the diffracted waves are in phase, application of trigonometry gives:

$$n\lambda = d \sin \alpha$$

$n$ is called the order of diffraction. When $n = 0$, 0th order diffraction occurs and $\alpha$ must be 0. When $n = 1$, 1st-order diffraction occurs; when $n = 2$, 2nd-order diffraction occurs, and so on. As $n$ increases, the angle between the diffracted wavefront and the row of atoms increases. The maximum value of $n\lambda$ corresponds to $\sin \alpha = 1$ (when $\alpha = 90^\circ$), so $n\lambda$ must always be less than $d$. Because $n \geq 1$ and $\sin \alpha$ cannot be greater than 1, $\lambda$ must be less than or equal to $d$ for diffraction to occur. These limits explain why atoms in crystals do not diffract visible light: the wavelengths of light are too long compared with the atomic spacings.
The preceding discussion assumed that an incident X-ray beam struck a row of atoms at 90°, but this is rarely the case. When the incident radiation strikes a row of atoms at another angle, coherent diffraction will still occur in any direction where X-rays are in phase (Figure 12.14a). To analyze this situation, we need only consider two rays (Figure 12.14b). They will be in phase if the difference in their path lengths, the difference between paths ABCD and EFGH, is an integral number of wavelengths \( n\lambda \). For the geometry shown in Figure 12.14b, we can easily verify that the rays will be in phase when:

\[
d (\sin \alpha' - \sin \alpha) = n\lambda
\]

where \( d \) is the atomic spacing, \( \alpha' \) and \( \alpha \) are the angles of the diffracted and incident wave with the row of atoms, \( n \) is the order of diffraction, and \( \lambda \) is the wavelength. This is the general equation for diffraction by a row of atoms in 2D space. Von Laue was the first to derive this equation, and he
derived similar equations for diffraction by three-dimensional structures. We call these the Laue equations.

W. L. Bragg developed a simpler mathematical treatment describing diffraction. His final equations are just as valid as von Laue’s, but the derivations avoided some unnecessary complexities. Although diffraction and reflection are two different processes, Bragg noted that diffracted X-rays behave as if they were reflected from planes within a crystal. To model this “reflection,” Bragg considered two parallel planes of atoms separated by distance $d_{hkl}$ (Figure 12.15).

![Bragg’s Law](image)

12.15 Bragg’s Law

The blue lines in Figure 12.15 represent parallel monochromatic X-ray beams striking and reflecting from two $(hkl)$ planes of atoms planes. The angle of incidence and the angle of reflection are both $\theta$. The geometry in the inset photo shows how we can calculate the extra distance followed by the bottom ray. The path lengths of the two beams must vary by an integral number of wavelengths if diffraction is to occur. So, the extra path distance followed by the bottom ray must equal $n\lambda$, and:

$$n\lambda = 2d_{hkl} \sin \theta$$
We call the equation above *Bragg’s Law*. Bragg demonstrated that we need not consider situations in which incident and diffraction angles are different (Figure 12.16a). Because we can always describe diffraction using reflection geometry, although diffraction and reflection are different phenomena. The angle of “reflection” $\theta$ is related to the incident angle ($\alpha$) and the diffraction angle ($\alpha'$) by

$$\theta = (\alpha - \alpha')/2$$

Examination of Bragg’s Law reveals that if we double the value of $n$ (the order of diffraction) and we double the value of $d_{hkl}$, $\theta$ will not change (diffraction will occur at the same angle.) So, 1st-order diffraction by planes with spacing $d_{hkl}$ occurs at the same angle as 2nd-order diffraction by a set of planes spaced twice as far apart. Figure 12.16b shows this relationship. Because we have no way to know diffraction order ($n$) when conducting routine X-ray studies, assuming 1st-order is simplest. In other applications of Bragg’s Law, the order of diffraction is important.

For more about Laue patterns, Bragg’s Law and diffractograms, watch these videos:
12.1.6 Diffraction by Planes of Atoms

A regularly spaced line of atoms provides a simple model for describing diffraction (Figure 12.17a). However, in two dimensions crystals contain multiple identical unit cells. So, crystals have many identical lines of atoms, all causing diffraction at the same angles (Figure 12.17b). In three dimensions, a crystal contains many identical 3D unit cells, all containing planes of atoms that cause diffraction at the same angles (Figure 12.17c). A distance $d_{hkl}$ separates the planes of atoms, and they diffract at angles we can calculate with Bragg’s Law. Although not clearly shown in Figure 12.17c, diffracted X-rays are not constrained to a plane but may go in any direction in 3D space.
12.18 Miller indices and the distance between planes

As discussed in Chapter 11, crystallographers use Miller indices \((hkl)\) to describe planes of atoms in crystals. \(d_{hkl}\) is the perpendicular distance between \((hkl)\) planes. Let’s consider planes perpendicular to this page.

Figure 12.18a shows a single (120) plane. Every unit cell is identical, so Figure 12.18b shows an entire family of (120) planes separated by the perpendicular distance \(d_{120}\). Different families of planes, with the same orientation but different indices, have different \(d\)-values. Figure 12.18c shows the family of (240) planes; they parallel (120) but are half as far apart. For all crystal systems, \(d_{120}\) is twice \(d_{240}\). Planes with higher numbers in their Miller indices are closer together than planes with lower numbers, and in general:

\[
d_{hkl} = n \, d_{h'k'l'}
\]

where \(h' = nh\), \(k' = nk\), and \(l' = nl\).
The relationship between Miller indices, unit cell lengths \((a, b, c)\), and \(d\)-values depends on the crystal system. Box 12.1 gives equations relating unit cell parameters to \(d\)-values. Derivation of equations for orthogonal systems (cubic, tetragonal, and orthorhombic) is simple compared with derivations for the other systems. For orthogonal systems:

\[
\begin{align*}
d_{100} &= a \\
d_{010} &= b \\
d_{001} &= c
\end{align*}
\]

For the other systems, we must also consider the angles \(\alpha\), \(\beta\), and \(\gamma\). Figure 12.19 shows this by comparing \(d\)-values with unit cell lengths for square, rectangular, and monoclinic cells. For the orthogonal cells, \(d_{100} = a\), but for the monoclinic cell it does not.
12.1.7 Routine X-Ray Analysis: Powder Diffraction

Mineralogists use two fundamental X-ray diffraction techniques: powder diffraction and single-crystal diffraction. Powder diffraction is much more common; we use it for routine mineral identification and for determining unit cell dimensions. We can also sometimes use this technique to learn
the proportions of different minerals in a rock or other mineral mixture. Single crystal diffraction, on the other hand, provides information necessary for determining a crystal’s space group and the arrangement of atoms in a crystal’s unit cell. We do not normally use powder diffraction to figure out atomic arrangements in crystals because powder diffraction data are more ambiguous for this purpose than single crystal data. Different X-ray peaks correspond to different crystals in the powdered sample, and the data do not reveal the orientations of crystals or planes causing diffraction. The Rietveld method, an extension of normal powder diffraction analysis, sometimes overcomes these complications.

For now, we will focus our discussion on powder diffraction and return to single-crystal techniques later. Figure 12.20 shows a typical powder diffractometer. The cabinet is about 2 meters tall.

12.21 A sample holder being loaded with a powdered sample

To prepare a sample for powder diffraction, we grind it to a fine powder. The goal is to have a near-infinite number of fine crystallites in random orientations. We load the powder into holders, such as the one in Figure 12.21 or put it on a glass slide. When lots of crystals in different orientations are X-rayed, many crystals will satisfy Bragg’s law for every set of \((hkl)\) planes. Thus, when an X-ray beam hits the sample, hundreds or thousands of diffracted beams will go in different
directions. Some diffracted beams will have high intensity and others will have medium or low intensity.

Consider a powdered sample of some mineral with (111) planes having a $d$-value of 5.0 Å. For Cu $K\alpha$, then, Bragg’s Law tells us this will cause diffraction at a $2\theta$ angle of 17.74°. When we X-ray the sample, many crystals will be oriented to cause diffraction at 17.74° to the incident X-ray beam. Figure 12.22a shows this in two dimensions. But, diffraction can go in any direction at 17.74° to the beam and, consequently, diffracted beams create a *diffraction cone* in three dimensions (Figure 12.22b).

In most crystals, a large number of $d$-values cause measurable diffraction. Each produces a cone at a different $2\theta$ angle to the X-ray beam. Figure 12.22c shows a small number of cones corresponding to different $d$-values — minerals typically produce many more than shown here. The cones are all concentric with the direct X-ray beam.
12.23 X-ray diffraction geometry and a modern diffractometer

Because we powdered the sample and get diffraction cones instead of separate rays going in discreet directions, we do not have to measure angles and intensities in 3D space. Some diffractometers are slightly different, but Figure 12.23a shows the basic geometry of diffraction. The photo in Figure 12.23b shows a modern diffractometer with this geometry. Besides an X-ray source (tube) and a detector (which measures the intensity of diffracted X-ray beams), the device includes several collimators and filters that enhance analysis.

In most diffractometers, the sample is at a fixed location (although it may be rotated by a device called a goniometer). The tube and detector, move in a planar circular arc, usually vertically, to measure diffraction intensities for 2θ values from very low angles to some high value. In practice, most diffractometers cannot measure peaks at angles below 1 or 2° 2θ because the direct X-ray beam bombards the detector. The upper 2θ limit of measurement usually depends on the need of
the mineralogist, but for most purposes we do not need data above 60° to 70° 2θ.

During analysis, the incident X-ray beam strikes the sample at many different θ angles while the detector moves to maintain Bragg Law (reflection) geometry. The angle of incidence and the angle of reflection are the same, so after being diffracted an X-ray beam travels at an angle of 2θ from the incident beam. Because a crystal contains many differently spaced atoms, diffraction occurs at many 2θ angles.

If a diffracted beam is to hit the detector, two requirements must be met:

- A family of planes with \(d_{hkl}\) must be oriented at an angle (θ) to the incident beam that satisfies Bragg’s Law.
- The detector must be at the correct angle (2θ) from the incident beam to intercept the diffracted X-rays.

Because the angle between the detector and the X-ray beam is 2θ, mineralogists usually report X-ray results as peak intensities for different 2θ values. For example, reference books list the two most intense diffraction peaks of fluorite (using Cu Kα radiation) as 28.3° and 47.4° 2θ. We must remember to divide 2θ values by 2 before we use them with Bragg’s Law to calculate \(d\)-values.

12.1.8 Data and Processing

When we X-ray a powdered sample, we obtain a powder diffraction pattern. The key information from the pattern is a list of \(d\)-values with diffraction intensities. Each \(d\)-value corresponds to sets of planes, and the intensity is a measure of how many atoms are on those planes. Because different minerals have different atomic arrangements, they yield different patterns.

Computers controlling powder diffractometers collect and
process data automatically. They compare diffraction results with data bases to identify the mineral or minerals present. The most comprehensive reference, the *X-ray Powder Diffraction File (PDF)* compiled by the International Centre for Diffraction Data, is available in computerized databases and contains information on almost 6,000 minerals and tens of thousands of other inorganic and organic crystalline compounds.

Simple mineral identification may require only a few minutes. For extremely precise results, however, data collection may take hours or longer. However, a shortcoming of computer interpretations is that they are “black box” procedures; they do not improve our knowledge or understanding of powder diffractometry and may occasionally produce misidentifications. And, for mixes of more than one mineral, computer programs always give an analysis but it is sometime difficult to evaluate the accuracy of the results.

To visualize diffraction measurements, we typically look at a *diffraction pattern* like the one below in Figure 12.24. It shows a diffraction pattern, also called a *powder pattern*, or a *diffractogram*, for halite. In standard diffraction patterns like this one, the X-axis is 2θ in degrees and the Y-axis is the intensity of diffraction. Following Bragg’s Law, $d$-value is infinite at 0° 2θ but decreases quickly with increasing angle. It is less than 20 Å at 5° 2θ, and then falls slowly to about 1 Å at 90° 2θ.
12.24 Diffractogram for halite

The peaks in Figure 12.24, also called reflections, are labeled with the 2θ angles at which diffraction occurs. They are also labeled with associated hkl indices, called Laue indices, and d-values. By convention, when talking about diffraction directions, we use Laue indices with no parentheses (because we are labeling a reflection and not a family of planes) as is done in this figure. Note that, according to Bragg’s Law, the peak labeled 222 (at 56.48°) in Figure 12.24 may be due to 1st-order diffraction by (222) planes (that have a spacing of 1.628 Å). However, 2nd-order diffraction by (111) planes (that have a spacing of 3.257 Å) also occurs at the same angle (discussed at the end of section 12.1.5, above). Higher-order diffraction from other families of planes, too, can cause diffraction at 56.48°. Because we have no way to distinguish 1st-order from higher-order diffraction, we label the peak 222, assuming 1st-order. So, Laue indices are not the same as Miller indices, but are close.

We always assign the strongest peak an intensity of 100% and calculate other intensities compared with that peak. In this pattern, halite’s 200 peak at 31.7° is most intense (100%). The
220 peak (45.5°) is about 35% as intense, and other peaks are all small. Minerals with high symmetry, such as halite (which is cubic), generally have fewer than 30 measurable reflections in their powder patterns. Minerals of low symmetry have more.

12.1.9 Effects of Different X-ray Wavelengths

All X-ray patterns seen in this chapter were obtained using a copper X-ray tube that produced Cu Kα radiation with wavelength 1.5418Å. Sometimes mineralogists use other kinds of tubes that produce a different X-ray wavelength. If so, the angles of diffraction will be different. The diffraction pattern will look the same but will be systematically shifted to higher or lower 2θ values. Nevertheless, when we calculate d-values using Bragg’s Law, the values come out the same no matter the X-ray tube and radiation used.

12.1.10 Intensity of Diffraction

When discussing planes in unit cells, h, k, and l may have any integer values, which implies the possibility of an infinite number of \(d_{hkl}\) values that could satisfy Bragg’s Law. However, intense diffraction will only occur if many atoms occupy the \((hkl)\) planes; without atoms no electrons are present to scatter X-rays. So, while Bragg’s Law tells us the angle at which diffraction could occur for any particular \(d_{hkl}\) value, it does not tell us anything about diffraction intensity.

Mineral unit cells contain a finite number of atoms, which restricts the number of d-values corresponding to planes of high atomic density. Therefore, the number of angles at which intense diffraction occurs is limited. An example in two dimensions will make this point.
12.25 Hypothetical arrangement of atoms in a 2D crystal

Consider the hypothetical unit cell shown in Figure 12.25a. All atoms are on top and bottom edges. The unit cell has dimensions of $a = 3.0\,\text{Å}$ and $b = 5.0\,\text{Å}$. Ignoring the third dimension (or assuming that all planes are perpendicular to the page), we can say that $d_{100} = 3.0\,\text{Å}$ and $d_{010} = 5.0\,\text{Å}$.

If we imagine a structure made of many of these unit cells (Figure 12.25b), we see that many atoms are in rows $5.0\,\text{Å}$ apart, and diffraction corresponding to $d_{010}$ ($5.0\,\text{Å}$) should be quite intense. We can also expect apparent diffraction by the (020) planes ($d = 2.5\,\text{Å}$) to be intense, although no atoms occupy every other (020) plane. This is because we have no way of knowing diffraction order, and 2nd-order ($n = 2$) diffraction by (010) planes occurs at the same angle as 1st-order diffraction by (020) planes. So we will identify 2nd order (010) diffraction as (020).

Besides (010) and (020), 200 diffraction ($d_{200} = 1.5\,\text{Å}$) will be quite intense because many atoms occupy the (200) planes. Note also that the (210) plains (diagonal in the figure) contain many atoms and should diffract almost as much as the (200) planes. Applying the equation in Box 12-1 above, we find that $d_{210} = 1.43\,\text{Å}$, just about the same as $d_{200}$. 
For our hypothetical crystal, (010) planes will cause very strong diffraction. (210), (200), and (020) planes will also cause significant diffraction. Applying Bragg’s Law to these \( d \)-values (see the table) tells us that the strongest diffraction will occur for a \( 2\theta \) value of 29.8°. Strong diffraction will occur for \( 2\theta = 65.2^\circ, 61.9^\circ, \) and 35.9°. But many other planes in this crystal will produce moderate or weak diffraction too.

### 12.1.11 Intensity of Diffraction: Halite

12.26 Atomic arrangement in halite and some planes in a unit cell

The preceding discussion was about a hypothetical 2D mineral. For a 3D example, let’s reconsider halite. Drawings \( a \) and \( b \) in
Figure 12.26 show two different depictions of the atomic arrangement in halite. The diagrams in the bottom of the figure highlight (in red) some of the (111), (200), and (220) planes.

Halite is cubic and has lots of symmetry. Consider the (200) planes shown in drawing 12.26d. Equivalent planes with equal spacing (not shown) can be parallel to the top and bottom faces, or parallel to the front and back faces. We omitted them for clarity. So, these drawings only show a few of many equivalent planes with equal $d$-values. In total, a cubic crystal like halite contains 12 different orientations for planes equivalent to (111), 9 different orientations for planes equivalent to (200), and 18 different orientations for planes equivalent to (220). If we X-ray halite, diffraction by (111) planes is relatively weak. The (200) and (220) planes produce the most intense reflections because there are many of those planes and they contain many atoms (as seen in the atomic drawings in this figure). You can verify this by looking at the diffraction pattern for halite in Figure 12.24.

12.1.12 X-ray Patterns, Symmetry and Mineral Identification
Different minerals produce different diffraction patterns because patterns depend on mineral composition and on the locations of atoms in unit cells. So, space symmetry, which relates to atom location, has great influence on diffraction patterns. Crystals with high symmetry contain identical planes of atoms in multiple directions. Consequently, fewer \( d \)-values cause diffraction – there are fewer diffraction peaks – than for crystals with low symmetry. And for crystals with high symmetry, X-ray peaks may seem somewhat regularly spaced on diffractograms. In contrast, low crystal symmetry means diffraction occurs in many more directions and diffraction patterns are irregular.

Figure 12.27 shows diffraction patterns for fluorite, quartz, and fayalite. Fluorite is cubic, quartz is hexagonal, and fayalite is orthorhombic. So, crystal symmetry decreases
downward in the figure. The number of reflections increases from fluorite to quartz to fayalite, and the patterns for fluorite and quartz appear to have a more even spacing of peaks.

An experienced crystallographer can often tell the crystal system with one look at a diffraction pattern, even if they do not know what the mineral is. This is most easily done for high-symmetry systems (such as cubic, hexagonal, or orthorhombic) and may be impossible for monoclinic or triclinic patterns. Experienced crystallographers also learn to identify common minerals quickly. Quartz, for example, has a strong peak at 20.8° 2θ, a stronger peak at 26.6°, and no other significant reflections (Figure 12.27b). That is enough to identify it. Graphite also has few peaks with its strongest at about 26.7°, but it lacks a peak near 20.8°. Calcite has a very strong peak just below 30°. And many other minerals have specific peaks that crystallographers quickly spot.

Even if we cannot identify a mineral with a quick look, we can
sometimes figure out the general kind of mineral that was X-rayed. For example, many minerals have no X-ray peaks below 20° 2θ, and most minerals have no peaks below 10°. But clay minerals have broad peaks in the 5° to 7° range, and phlogopite and other micas have very large peaks at around 9° 2θ. Figure 12.28 shows an example pattern for phlogopite, a mica; the strongest peak is at 8.7°. Diffraction patterns for amphiboles, too, have a distinguishing characteristic – a double peak at 10-11° 2θ characterizes tremolite and most other amphiboles. Figure 12.28b shows a typical diffraction pattern for an amphibole.

The low-angle reflections produced by clays and micas correspond to large d-values. The large values are due to the layered atomic arrangements in these mineral groups. The repeat distance between layers, called the basal spacing, is around 10 Å in most micas and repeat distance can be significantly greater in clays. The unit cells for most other kinds of minerals are too small to permit such large repeat distances and large d-values. So, if crystallographers see peaks at or below 10°, they often know what general kind of mineral they have.

12.1.13 Extinctions
12.29 Destructive interference and extinction

Sometimes, due to destructive interference, planes containing many atoms do not produce diffraction. We term this phenomenon a systematic absence, or an extinction. Figure 12.29a shows a two-dimensional drawing of a structure in which atoms occupy the corners (grey atoms) and the center (red atoms) of each unit cell. As shown in Figure b, when 010 diffraction occurs at angle $\theta$, beam $X$ and $Y$ are completely in phase. If the diffraction is 1st order, beam $Y$ travels exactly $1\lambda$ farther than beam $X$.

However, the constructive interference cannot prevail when we
account for the (red) atoms between the (010) planes. X-rays scattered by these atoms travel $\frac{1}{2} \lambda$ more or less than those scattered by the adjacent (010) planes. This produces waves that are out-of-phase and we get perfect destructive interference, shown in Figure c. No X-rays will be found at the angle $\theta$ although it satisfies Bragg’s Law for $d_{010}$. This effect is extinction, and we would say the 010 diffraction peak is extinct.

Although (010) planes do not diffract, (020) planes do. But the smaller $d_{020}$ compared with $d_{010}$ results in the larger diffraction angle shown in Figure d. The atomic arrangement we saw earlier in this chapter in Figure 12.25 also produces extinctions. 100 diffraction is absent because additional atoms occur halfway between the (100) planes.

Figures 12.25 and 12.29 show two-dimensional examples of structures that result in extinctions due to end-centered and body-centered unit cells. In three dimensions, end-centered, body-centered, and face-centered arrangements also produce extinctions. We often describe extinctions using arithmetical rules. For body centering, the rule is that an $hkl$ peak will only be present if $h + k + l$ is an even number.

Besides centering, screw axes and glide planes also cause extinction because they, like centering, result in planes of atoms between other planes. The systematic extinction of certain X-ray peaks, then, is one way we figure out space group symmetry. Box 12-2 gives more examples of extinction rules.
Lattice centering can cause X-ray extinctions. Screw axes and glide planes do too. Arithmetical rules involving \( h, k, \) and \( l \) describe which peaks can be present. (Although called *extinction rules*, the rules usually describe which peaks are present, not which peaks are extinct.)

The table below lists the affected peaks and gives rules for their presence. This table includes only some of the many possible screw axes. Rules for other screw axes can be inferred by analogy with the ones listed here.

For lattice centering, extinction rules affect all \( hkl \) reflections. But screw axes and glide planes only affect some. For example, as listed in the table below, a 2\(_1\) screw axis parallel to the \( a \)-axis causes extinction of \( h00 \) peaks if \( h \) is an odd number. If \( h \) is an even number, the peak will be present, and other (not \( h00 \)) peaks are not affected at all.

<table>
<thead>
<tr>
<th>Symmetry Element</th>
<th>Affected Reflection</th>
<th>Condition for Reflection to Be Present</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice Centering</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>primitive lattice (P)</td>
<td>( hkl )</td>
<td>always present</td>
</tr>
<tr>
<td>body-centered lattice (I)</td>
<td>( hkl )</td>
<td>( h + k + l = ) even</td>
</tr>
<tr>
<td>end-centered lattice (A)</td>
<td>( hkl )</td>
<td>( k + l = ) even</td>
</tr>
<tr>
<td>end-centered lattice (B)</td>
<td>( hkl )</td>
<td>( h + l = ) even</td>
</tr>
<tr>
<td>end-centered lattice (C)</td>
<td>( hkl )</td>
<td>( h + k = ) even</td>
</tr>
<tr>
<td>face-centered lattice (F)</td>
<td>( hkl )</td>
<td>( h, k, l ) all odd or all even</td>
</tr>
<tr>
<td><strong>Screw Axes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-fold screw, 2, parallel to ( a )</td>
<td>( h00 )</td>
<td>( h = ) even</td>
</tr>
<tr>
<td>4-fold screw, 4, along parallel to a</td>
<td>( h00 )</td>
<td>( h = ) even</td>
</tr>
<tr>
<td>6-fold screw, 6, parallel to ( c )</td>
<td>( 00l )</td>
<td>( l ) divisible by 3</td>
</tr>
<tr>
<td>3-fold screw, 3(_1) or 3(_2), parallel to ( c )</td>
<td>( 00l )</td>
<td>( l ) divisible by 3</td>
</tr>
<tr>
<td>6-fold screw, 6(_2) or 6(_4), parallel to ( a )</td>
<td>( h00 )</td>
<td>( h ) divisible by 4</td>
</tr>
<tr>
<td>4-fold screw, 4(_1) or 4(_3), parallel to ( a )</td>
<td>( h00 )</td>
<td>( h ) divisible by 4</td>
</tr>
<tr>
<td>6-fold screw, 6(_1) or 6(_5), parallel to ( c )</td>
<td>( 00l )</td>
<td>( l ) divisible by 6</td>
</tr>
<tr>
<td><strong>Glide Plane Perpendicular to the B-axis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a glide</td>
<td>( h0l )</td>
<td>( h = ) even</td>
</tr>
<tr>
<td>c glide</td>
<td>( h0l )</td>
<td>( l = ) even</td>
</tr>
<tr>
<td>n glide</td>
<td>( h0l )</td>
<td>( h + l = ) even</td>
</tr>
<tr>
<td>d glide</td>
<td>( h0l )</td>
<td>( h + l ) divisible by 4</td>
</tr>
</tbody>
</table>
To see the importance of extinctions, consider almandine, a garnet. Almandine is cubic and its crystals have symmetry $4/m32/m$. But the atomic arrangement has a body centered unit cell, a screw axis ($4_1$), and two glide planes ($a$ and $d$); it belongs to space group = I $4_1/a32/d$.

For cubic minerals we can calculate $d$-values from the relationships in Box 12-1:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

So, we can calculate $d$-values for all combinations of $h$, $k$, and $l$. If we only consider combinations that could give X-ray peaks for $2\theta < 90^\circ$, we get 726 possibilities. That is a lot. However, when we apply the extinction rules for body centering, the screw axis, and the two glide planes, most reflections go away. We are left with only 51 possibilities! And some of these correspond to planes that contain no, or few, atoms – so they produce no reflections.

The diagram below (Figure 12.30) shows a standard reference pattern for almandine. It contains fewer than 15 visible peaks. Some appear spaced regularly, but gaps (missing peaks) correspond to extinctions.
12.30 Diffraction pattern for almandine

12.1.14 Indexing Patterns and Determining Cell Parameters

We have labeled the peaks on the X-ray pattern in Figure 12.30 with $hkl$ indices corresponding to the planes causing diffraction. For identifying unknown minerals, we do not need to know which $hkl$ indices correspond to which $d$-values, but for other purposes, such as determining unit cell dimensions, we must.

The process of matching $d$-values to $hkl$ indices is called indexing. The easiest way to index a pattern — unless a computer does it — is to compare it with one for a similar mineral already indexed. For instance, if we measure a pattern of an unknown garnet, it will have the same general appearance as the one in the figure above, so we can easily assign $hkl$ indices to the peaks. This is quick and simple. Without a pattern to compare, the process becomes more complex and, except perhaps for cubic minerals, computer programs are desirable or necessary. In the past it was different, but today analyzing a diffraction pattern is automated. With $d$-values for many peaks (the more the better), computer programs use the equations in Box 12.1 and a least-squares approach to derive the six cell parameters ($a$, $b$, $c$, $\alpha$, $\beta$, $\gamma$). The programs then assign $hkl$ indices to each peak.

12.1.15 Uncertainties

Powder diffraction is not always an exact process, and several things may cause X-ray patterns to deviate from those in reference files. Proper sample preparation is crucial to obtaining accurate patterns. Complications arise when we do not grind a sample properly, or when powdered crystals are not in truly random orientations. For example, because micas are hard to grind and their tiny flakes may align parallel to each
other, obtaining random orientation and a good X-ray pattern is difficult for micas. A second problem is that compositional variations can affect X-ray patterns (see Box 12-3 below). Despite these complications, the PDF data contains adequate reference patterns for most mineralogical uses.
Box 12-3 Compositional Control on Diffraction Patterns

Powder patterns for quartz, fluorite, and other minerals with fixed compositions vary little from those in reference databases. This is not the case for minerals that form solid solutions.

For example, consider plagioclase. Figure 12.31 in this box shows X-ray patterns for albite and anorthite, the two main plagioclase end members. Unit cell parameters for each are also given. These two minerals have almost, but not quite, the same unit cell size and shape. They also have atoms in the same places within their unit cells. So the two patterns have peaks at about the same angles. (You may have to look closely to see this because albite and anorthite are triclinic which means the patterns are a bit chaotic.)

Peak intensity, however, is significantly different for the two feldspars. This difference is because the minerals have different compositions. The same \((hkl)\) planes cause diffraction, but because atoms on those planes are different elements, diffraction intensity by the planes is different. Plagioclase feldspars can have any composition between albite and anorthite and consequently may produce many different looking diffractograms.

12.31 Comparing diffraction patterns for albite and anorthite
12.1.16 Single Crystal Diffraction

12.32 A single crystal diffractometer

For powder diffraction, we grind a sample so we have many crystallites contributing to the diffraction pattern. Single-crystal diffraction instead, as the name implies, uses only a single crystal. The technique involves measuring directions and intensities of diffraction when a collimated X-ray beam strikes a carefully oriented small crystal. Crystals are typically 50 to 250 microns (0.05 to 0.25 mm) in longest dimensions. The diffractometer rotates the crystal and moves the detector to measure intensities of all diffraction peaks in 3D space. Typically, a detector moving in a sphere or hemisphere around the crystal measures diffraction intensity. Figure 12.32 shows an example of such a diffractometer. Data collecting can be time-consuming, but modern single crystal diffractometers are computer controlled and can collect diffraction intensities for thousands of directions — sometimes as many as 20,000 — in a few hours. Computers store the data and process it automatically.

We use the data obtained from single-crystal diffraction studies to determine crystal structures. If we know the composition of a mineral, we know how many atoms of which elements are present in a unit cell. Computer programs figure out where atoms are relative to each other, based on the diffraction data. We call this process a crystal structure.
determination or crystal structure refinement. Crystal structure determination involves many complexities, but automation and high-speed computers have simplified the process considerably since the Braggs determined the first crystal structure in 1913.

12.2 Obtaining a Mineral Analysis

X-ray diffraction has historically been, and still is, a very important technology used by mineralogists. It also has important applications in solid-state physics, biophysics, medical physics, chemistry, and biochemistry. It allowed Watson and Crick to discover the structure of DNA in 1953. Yet, diffraction rarely tells us what elements a mineral contains, instead telling us how atoms are arranged. So, petrologists and mineralogists use other approaches to obtain chemical analyses.

Until about 1960, geologists obtained mineral and rock analyses primarily using an approach called “wet chemistry.” To obtain a wet chemical analysis, we can dissolve samples in acid and then analyze them by reactions involving precipitation, titration, or colorimetry. **Gravimetric analysis** involves reacting the acid solution with reagents to produce a precipitate. We then weigh the precipitate, and the weight tells how much of an element of interest was present in the original sample. **Volumetric analysis** involves titrating the sample until a specific reaction occurs. The volume of reagent necessary to make the reaction occur is proportional to the amount of the element of interest that is present. **Colorimetric analysis** involves reaction with a reagent that changes the color of the solution. The color intensity is proportional to the amount of the element of interest present, which we quantify by comparison to standards. The advantage of wet chemical analysis is that we can analyze just about any element. However, different elements require different approaches, the technique requires large samples that are
destroyed during analysis, and analyses are difficult and time-consuming to do with accuracy. For these reasons and because other, simpler techniques are now available for most purposes, wet chemical analysis is rarely done today.

In the 1960s, researchers developed several new kinds of instruments that made mineral and rock characterization and analysis easier, while also providing new and different kinds of information. Today, we use many different kinds of analytical techniques and devices; for a good summary, go to https://serc.carleton.edu/research_education/geochemsheets/browse.html. The development of electron microscopes and electron microprobes was of particular importance – we discuss these instruments below.

12.2.1 Electron Microscopes

Conventional microscopes use visible light to examine a small specimen, or sometimes a thin section. An electron microscope uses a beam of electrons instead of light. Electron microscopes can magnify samples thousands of times more than conventional light microscopes, allowing us to see very fine mineral grains and details. The greater magnification and resolution are possible because the effective wavelength of an
electron is much smaller than the wavelength of light. Consequently, electron optics can focus on much smaller areas than light optics.

There are several different kinds of electron microscopes; *scanning electron microscopes (SEMs)* are by far the most common. In a scanning electron microscope, such as the one shown in Figure 12.33, high energy (typically 15–20 keV) electrons are generated at the top of the column on the left. The electrons are focused into a narrow beam that scans back and forth (*rasters*) across a sample at the bottom of the column to produce an image. SEMs can scan very small areas, operating over a wide range of magnifications, up to 1,000,000x when properly optimized. They can resolve topographical or compositional features just a few nanometers in size. Several different kinds of images can be displayed on a monitor screen depending on the user’s needs.

### 12.2.1.1 SEM Images

Several important things occur as the electron beam interacts with a sample (Figure 12.34). Some electrons will reflect from the sample surface with no loss of energy. We call these electrons *backscatter electrons*. Additionally, ionization produces lower-energy *secondary electrons* when the original
high energy electrons interact with valence electrons in the sample. To obtain standard SEM images, a detector measures the intensity of secondary electrons (SE) emitted by the sample as the beam rasters across it. This allows creation of an image with brightness proportional to the number of electrons reaching the detector.

12.35 Secondary electron images of three SiO$_2$ polymorphs. The white bars are 0.01 mm long.

Most SEMs also have a separate detector for creating backscatter electron (BSE) images. For both SE and BSE images, the number of electrons emitted, and thus the brightness or darkness of an image, depends on sample topography and on the composition of the sample. The emission of secondary electrons is particularly sensitive to topography, and only slightly affected by composition. In contrast, the emission of backscatter electrons depends significantly on the composition of the sample. Heavier elements backscatter electrons more efficiently than light elements. So, BSE images show compositional variations within a sample as well as surficial features.

Figure 12.35 shows secondary electron images of very small
quartz, tridymite, and cristobalite crystals. These SiO$_2$ polymorphs all belong to different crystal systems and the mineral habits reflect the differences. SE and BSE images, like the images in this figure, sometimes look like conventional photographs but are not the same thing because they do not involve light reflection.

Figure 12.36 shows an example. This is a BSE image of an amphibolite that experienced complex metamorphic reactions. The reactions produced intergrowths of epidote and quartz called symplectites. The very small grains and textures would be hard to see in thin section (the bar scale is 0.25 mm long).

In this image, distinct contrast between white and shades of grey reflect mineral compositions. Dark colored minerals (quartz and plagioclase) are those that contain mostly elements with low atomic numbers. The light colored clinopyroxene and epidote contain significant amounts of heavier elements, in particular iron. The amphibole has an intermediate composition.

12.2.1.2 Secondary X-rays and Characteristic Radiation

An additional important phenomenon occurs when beam electrons hit atoms in a sample. The electrons cause the atoms to emit
characteristic secondary X-rays with energy that depends on the element. This process is much the same as the way that the target in an X-ray tube emits X-rays. If the sample contains several different elements, it may emit X-rays at multiple wavelengths corresponding to different energies. Because different elements give off characteristic X-rays with different energies, the emission spectrum displays the chemical composition of the specimen. Most SEMs are equipped with energy-dispersive X-ray detectors for measuring X-ray energies and, thus, for identifying elements in a sample. This analytical method is called energy-dispersive spectroscopy (EDS).

Iron, for example, emits its strongest characteristic radiation (called $K_\alpha$ radiation) at 6.4 keV. So, when struck by a beam of electrons, iron atoms emit energy at 6.4 keV, and the intensity of the emission is proportional to the amount of iron in the specimen. Iron also emits characteristic X-rays of other energies, but the intensities are much less than $K_\alpha$ radiation.

![EDS spectrum for biotite](image)

**12.37 EDS spectrum for biotite**

Energy dispersive detectors measure X-ray energy and intensity over a wide range of energies simultaneously. Spectra can be collected quickly, perhaps counting X-rays for just a few
seconds, to get an idea of the composition of a sample. For more accurate results, counting times must be longer. Figure 12.37 shows an energy spectrum for biotite. Some elements produce more than one peak but the strongest peak for any element is always $K\alpha$. This is a typical spectrum for biotite, but biotite varies in composition, so the relative heights of the peaks are not the same for all specimens.

A computer takes a spectrum such as the one in Figure 12.37 and quickly analyzes the intensities of all X-ray peaks to produce an EDS chemical analysis for the sample. EDS analyses are generally semiquantitative, but often that is all that we need for mineral identification.

### 12.2.2 Electron Microprobes

For the most accurate and precise chemical analyses, we use wavelength dispersive X-ray spectroscopy (WDS) instead of EDS. Special detectors called wavelength spectrometers measure the intensity of X-rays having specific wavelengths, characteristic of specific elements. Because most scanning electron microscopes (SEMs) do not have wavelength spectrometers, they cannot produce WDS analyses. Additionally, SEMs generally lack other features, common to electron microprobes, that lead to more accurate and precise analyses. These shortcomings may be disappearing today, as some SEM vendors have developed a new generation of wavelength spectrometers for their instruments.
Electron microprobes, more properly called electron probe micro analyzers (EPMAs), are instruments similar to SEMs but specifically designed for obtaining WDS analyses (Figure 12.38). Microprobes have a more intense electron beam than SEMs, and may have three or more spectrometers besides imaging and EDS analytical capabilities. However, we cannot obtain WDS analyses as quickly as EDS analyses because a spectrometer only measures one element at a time on each spectrometer. Additionally, accurate WDS measurements require standardization before analysis, or before each analytical session, adding additional time to the procedure.

The WDS approach is much more accurate than EDS and can detect elements present in smaller amounts, with precision about 1 to 2% of the amount present (for major elements). The analytical accuracy depends primarily on how well we have standardized the microprobe. Today’s microprobes can do all the same imaging that an SEM can do. The four monitors in Figure 12.38 allow viewing of different kinds of images and analytical data simultaneously.

Scanning electron microscopy and electron microprobe analysis have several major advantages over most other analytical
techniques and are therefore widely used. First, they allow us to examine rocks, mineral grains, or thin sections with little sample preparation. Second, microprobe analysis is a nondestructive analytical technique. So, we analyze samples without destroying them. Perhaps most important, microprobe analyses focus on very small spots. We can analyze single mineral grains, or many spots in the same grain, to look at very small-scale changes in chemistry. No matter the exact technique used, because the electron beam typically excites a sample volume of only 20 cubic microns, it can resolve very fine compositional features. Additionally, individual X-ray peaks may be isolated to construct elemental maps, showing the distribution of different elements in different parts of the sample.

One shortcoming of both EDS and WDS analysis is that elements with low atomic number are difficult to analyze. This problem arises because low-numbered elements emit X-rays of low energy. For several reasons, such X-rays may not make it to the detector or spectrometer, or may not be measurable once they get there. Technology varies, but some of the newest EDS detectors can now measure X-rays generated by beryllium and lithium, something impossible just a few years ago. WDS analysis can, in principle, analyze elements from Be to U but technical complications occur at both extremes.

An additional complication arises because most geological materials do not conduct electricity. Unless we coat them with a conducting material, static charge builds up, distorting images and analyses. So, we vaporize gold, carbon, or other conducting material in a vacuum and let it precipitate on our specimen. Gold coatings work very well for some applications, producing excellent images. However, we cannot easily remove the gold, and it interferes with analyses. So mineralogists and petrologists generally use carbon coating instead. Unlike gold, we can remove the carbon coating from a thin section by light polishing.
As an alternative to coating samples, we can reduce or eliminate charging problems by using an environmental scanning electron microscope (ESEM) instead of a standard SEM. ESEM is a technology that, unlike a conventional SEM, does not require that the sample be under a high vacuum. A small amount of gas (up to 20 torr/2.7 kPa) provides a medium to conduct electrons away from the sample. ESEMs require no sample coating and many permit examination of large samples, larger than conventional SEMs. The quality of images and analyses, however, is reduced compared with conventional SEMs.

### 12.2.3 Electron Backscatter Diffraction (EBSD)

Electron backscatter diffraction is an analytical technique that has existed for more than 20 years and is becoming quite popular today. This technique is based on the observation that electrons in an electron beam can be diffracted by atomic layers in crystals. The diffracted electrons create patterns (called *EBSP patterns*) that can be seen when the electrons hit a fluorescent phosphor screen. EBSP patterns reflect the atomic arrangement in a crystalline material, and so provide information about crystal structure and crystal orientation. Automated software can compare a pattern with patterns in a data base to identify crystalline materials based on crystal structure. The patterns can also be used for fabric analysis of crystal aggregates. One shortcoming of EBSD is, however, that it requires special sample preparation that can be time consuming.

### 12.2.4 Other Analytical Techniques

Mineralogists and petrologists use many other analytical techniques besides those described above. All are destructive techniques, and most are more useful for analyzing rocks than individual minerals because they require large samples. A fairly comprehensive list of analytical techniques can be
X-ray fluorescence (XRF) is a technique used mainly for analyzing rocks. It requires relatively large samples melted with a flux to make a glass disk. The disc is placed in the machine, where a high-energy X-ray beam hits it. Atoms in the sample fluoresce, producing characteristic X-rays that are analyzed using EDS or WDS detectors. We compare unknowns with well-characterized standards to obtain quantitative results.

Atomic absorption spectroscopy (AAS) is based on the absorption of light by an atomized sample. We dissolve samples in an acid solution or flux that we then introduce to a hot (2,000 °C/3,600 °F) flame or graphite furnace. The flame atomizes the liquid, converting it to a gas phase. We use special light sources to pass light of different wavelengths, characteristic of different elements, through the gas. We compare light absorption of unknown samples and standards to determine the concentration of the element of interest. We can use AAS to analyze most metals but not nonmetals.

Inductively coupled plasma (ICP) is used mostly to analyze rocks, not individual minerals. After we dissolve it in acid, or in a flux, we heat the sample in a plasma (6,000 °C/11,000 °F), ionizing its atoms. At 6,000 °C, the atoms emit light at wavelengths that depend on the elements present. We measure the intensity of light emission at different wavelengths to calculate the concentrations of each element present. ICP analysis is very sensitive and can measure elements present at the parts-per-billion level.

Inductively coupled plasma mass spectrometry (ICP-MS) is a variant of ICP analysis. Instead of analyzing the emitted
light, displaced ions are analyzed using a mass spectrometer to measure concentrations of individual isotopes. ICP-MS can be used with a laser that ionizes small spots on individual mineral grains. ICP-MS is very sensitive and can analyze many elements at concentrations as low as 1 part per trillion.

**Ion microprobes**, also called **secondary ion mass spectrometers (SIMS)**, analyze small spots (on the order of a few microns) on a sample. A focused beam of ions bombards the sample, burning a pit as it creates a plasma and releases ions. The ions then travel to a mass spectrometer for analysis. Ion microprobes are much more sensitive than electron microprobes and we use them to measure the concentrations of very light elements that we cannot analyze with a microprobe. However, standardization is problematic and limits accuracy.

**Mössbauer spectroscopy** is a limited but very valuable analytical technique. We use it to determine the oxidation state and coordination of Fe in minerals. A sample is exposed to gamma radiation emitted by an $^{57}$Fe source, and a detector measures how much of the radiation is absorbed by Fe as it passes through the sample. The gamma-ray source is accelerating back and forth, changing the energy slightly due to the Doppler effect. The absorption at different velocities (energies) reflects Fe valence and coordination number in the specimen. We could use Mössbauer spectroscopy to analyze a few other elements besides Fe, but none are generally of geological interest.

**Visible and infrared spectroscopy** is an analytical technique based on the absorption of visible light or infrared radiation (IR) by a sample. Samples are prepared in one of several ways to make them thin enough for light/radiation to pass through. We shine a beam of light through the sample and measure the absorption of different
wavelengths. Absorption of visible light can tell us the oxidation state and coordination number of important transition metals. Absorption of IR radiation helps identify minerals, and reveals the relative amounts of \( \text{H}_2\text{O} \) and (OH)\(^-\), or of \( \text{CO}_2 \) and (CO\(_3\))\(^{2-}\), in a specimen.

*Raman spectroscopy* is based on inelastic (Raman) scattering of light from a sample. A monochromatic laser beam is focused on a small spot on the sample, and most light photons bounce off with the same wavelength as the original light (elastic scattering). The few that do not will have slightly increased or decreased wavelengths and energies. The difference in energy, called the *Raman shift*, reflects the presence of specific ions and atoms in the sample. It also tells us the coordination numbers of some elements, helps distinguish polymorphs from each other, and provides a measure of the crystallinity of a specimen.

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12.1 An X-ray diffractometer, xrpd.eu
12.2 Röntgen at work in 1896, crtsite.com
12.3 Diffraction gratings, educatingphysics.com
12.4 Diffraction pattern of sphalerite, www.nature.com
12.6 X-ray tube, designworldonline-dot-com
12.8b Bee making ripples Bogdan Giusca, Wikimedia Commons
12.11c Ripples on lake, W.carter, Wikimedia Commons
12.20 A powder diffractometer, serc.carleton.edu
12.21 Powder diffraction sample holder, USGS
12.23b X-ray diffractometer, xrpd.eu
12.24 to 12.30 Diffraction patterns from rruff.info
12.32 Single crystal diffractometer, geo.arizona.edu
12.33 Electron microscope, jeolusa.com
12.35 SEM images, George Rossman
12.36 BSE image. Belyavin et al. (2014)
12.38 An electron microprobe, cameca.com

Video 12-1: Bragg’s Law and Diffractograms, Keith Purtirka, YouTube
Video 12-2: Laue patterns and Bragg’s Law, Keith Purtirka, YouTube