

X-Ray Diffraction (XRD)

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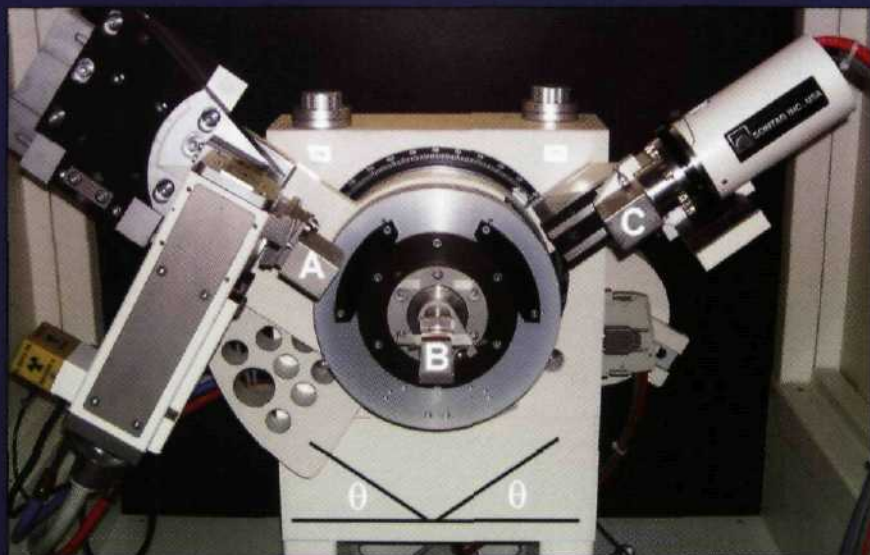


Figure 1. A Scintag[®] powder X-ray diffractometer, Miami University. As the X-ray source, A, and a detector, C, are scanned in a circular path (measured by the angle 2θ) around a stationary powder sample, B, X-rays are emitted from the source, diffract off a sample, and are collected by a detector. A computer receives the diffraction data from the detector and plots it as a diffraction pattern (fig. 2).

Every mineral has a specific crystal structure and chemical composition (although the latter is often variable within limits). In the May/June 2004 issue of *Rocks & Minerals* we looked at one of the most useful analytical tools for the characterization of minerals, energy dispersive spectrometry (EDS) (Rakovan 2004). As was noted, EDS is used for the analysis of mineral chemistry. In contrast, the most utilized tool for the characterization of a mineral's crystal structure is X-ray diffraction (XRD). Without getting into the details of how diffraction occurs (a good series of articles that covers the details is Arem 1971a,b,c), it is useful to know something about what XRD can tell you and its applications in mineralogy.

An instrument that is used to collect XRD data is called a *diffractometer*. There are many different types of diffractometers; these vary in the mechanics of data collection and methods of data recording. Two general categories of diffractometers are those that collect data from single crystal fragments and those that are used to analyze powder samples (fig. 1).

Powder XRD is the most widely utilized because of the ease with which it is performed and because it is a quick and accurate way to identify a mineral or mixture of minerals.

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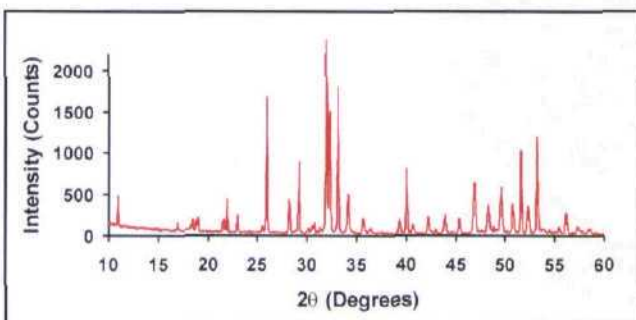


Figure 2. A powder X-ray diffraction pattern from fluorapatite. The peaks in the pattern are due to diffraction of X-rays off planes of atoms within crystals from a powder sample. The angular position of each peak (2θ) can be used to calculate the spacing between planes within the structure using Bragg's equation. This pattern is unique to fluorapatite and thus can be used as a "fingerprint" in its identification by comparison to a database of known patterns.

Figure 2 is a powder diffraction pattern from fluorapatite. The position of the peaks in this pattern and their relative intensities are unique to fluorapatite and thus can be used as a "fingerprint" for its identification. A unique XRD fingerprint is characteristic for all minerals; hence, the importance of XRD in mineral identification. Powder diffraction data can also be used for many other applications, including determination of the unit cell dimensions of a mineral, quantitative determination of the relative amount of different minerals in a mixture, and refinement (more precise

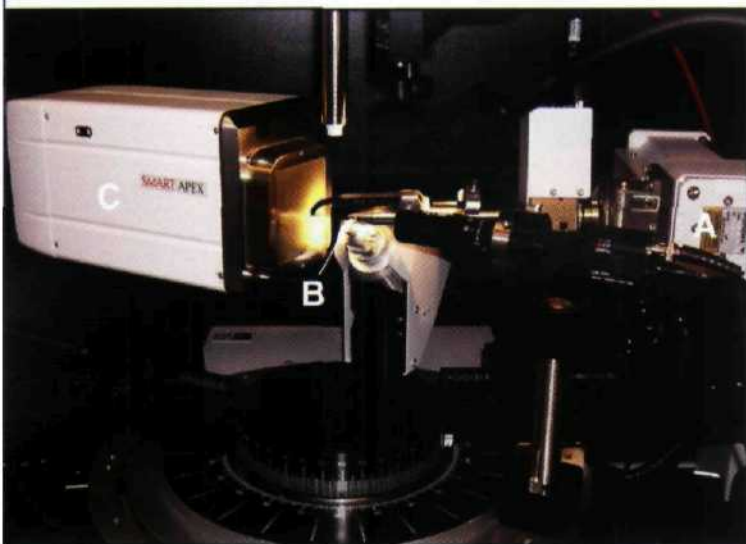


Figure 3. A Bruker APEX[®] single crystal diffractometer, Miami University. The X-ray source, A, the crystal, B, and the CCD detector, C, can be moved about three independent axes so that diffraction from all atomic planes within the crystal can be collected.

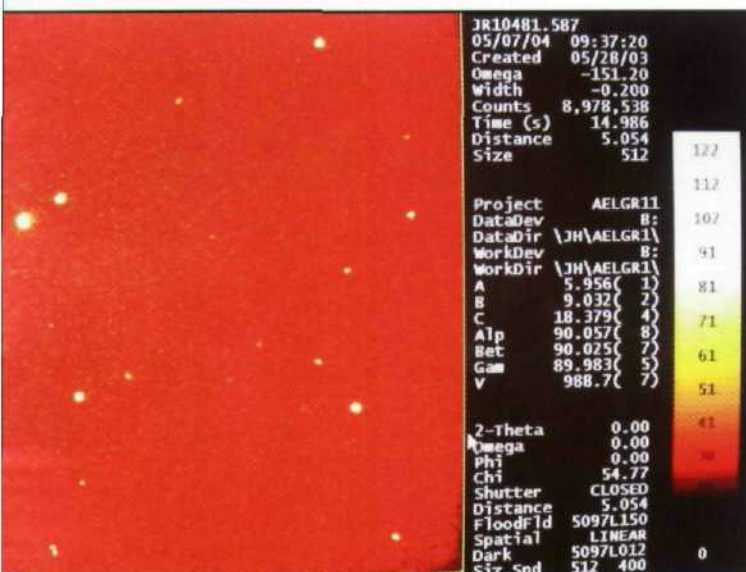


Figure 4. A digital single crystal X-ray diffraction photograph from fluorapatite taken with a Bruker APEX[®] diffractometer. Bright spots are where X-rays that were diffracted from the crystal intersected the CCD detector. A mathematical transform of the angular position and intensity of the diffraction spots from a crystal yields a map of the electron density within the crystal and allows for the determination of its atomic structure.

determination) of the arrangement of atoms within a mineral, if its general structure is already known. The most commonly used method for the latter application is the Rietveld method (Post and Bish 1989).

Data collected from a single crystal fragment, rather than a powder, are generally used to solve and refine the crystal structure of a mineral. In the past half-decade or so there has been a revolution in single crystal XRD with the advent of the use of charge-coupled devices (CCDs) as X-ray detectors in diffractometers. CCDs employ the same technology

used in almost all digital cameras today. Figure 3 shows an example of such an instrument, and figure 4 is a single frame (essentially a digital photograph) of diffraction data from a single crystal of apatite. The bright spots in this image are the result of X-rays diffracting off atomic planes within the crystal and onto the CCD camera. They are basically equivalent to the peaks in the powder pattern shown in figure 2. The ease of data collection with a CCD single crystal diffractometer, compared to older scintillation detectors that would only collect one diffraction spot at a time, has made it practical to use these instruments for other applications, including simple phase identification and unit cell determination. One interesting capability is the combination of optical and X-ray goniometry (angular measurements) where one can accurately determine the Miller indices of crystal faces relative to the unit cell of the crystal that was previously refined from X-ray data.

Two of the more important characteristics of CCD detectors in XRD are their high sensitivity and area detection. Together, these allow for faster data collection, the capacity to analyze smaller crystals, and the collection of data at all angular positions. For example, it has been demonstrated that diffraction data can be collected from crystals many orders of magnitude smaller than previously possible (Burns 1998). Collection of data at all angular positions alleviates the problem of not collecting unexpected or "extra" diffractions that may arise from superstructures or lowering of symmetry. Indeed, since the introduction of CCD detectors in XRD, many mineral structures that were previously unsolved or were poorly constrained have been refined to great accuracy (i.e., Hughes et al. 2003). Because XRD was the first, and remains the most important, tool for elucidating the atomic structure of materials, it is no exaggeration to say that its discovery in 1915 marked the advent of modern mineralogy and solid-state materials science. Not surprisingly, then, there are thousands of publications that give introductions to XRD. If you are interested in learning more about this technique, good summaries are found in Cullity and Stock (2001), Klug and Alexander (1974), and Reynolds (1989).

ACKNOWLEDGMENTS

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