

# APPENDIX 3

---

## ANCILLARY TECHNIQUES

---

A number of ancillary techniques are very commonly employed in conjunction with reflected-light microscopy in order to obtain more detailed information on the identities and compositions of phases. Two that are particularly important are X-ray powder diffraction and electron probe microanalysis, but other techniques are growing in importance. A detailed discussion of these methods is inappropriate here, but the techniques are sufficiently important that this appendix is included to suggest suitable references dealing with these topics in detail and to draw attention to some practical problems in applying the methods to material in polished sections.

### A3.1 X-RAY POWDER DIFFRACTION

The theory and applications of X-ray powder diffraction are described in numerous texts and papers (e.g., Zussman, 1977; Azaroff and Buerger, 1958; Nuffield, 1966). All X-ray diffraction methods result from the diffraction of a beam of X-rays by a crystalline material. The precise method most often used in conjunction with reflected-light studies is X-ray powder photography using the Debye-Scherrer camera. Here the powdered sample can be a small "bead" only a fraction of a millimeter in diameter mounted on the tip of a fine glass fiber. When the sample is mounted in the camera, it is aligned so that a pencil beam of X-rays entering through a collimator strikes the sample and is diffracted to produce a pattern of lines on a strip of photographic film. The positions of these lines can then be measured and the information converted to the separation between layers of atoms in the crystal structure. The X-ray powder pattern provides, in many cases, a "fingerprint" identification of the

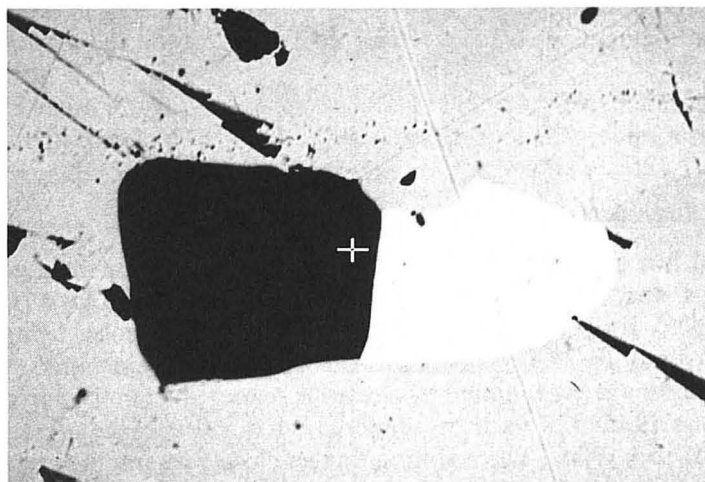
material. In certain cases, precise measurement of the pattern may also furnish compositional information [e.g., the iron content of a (Zn,Fe)S sphalerite or the Fe:S ratio of a pyrrhotite].

X-ray powder camera methods are particularly useful in ore microscopy because of the very small amount of material required. Small grains can be dug directly out of a polished section using a needle or special diamond pin “objective” and rolled up into a ball of collodion, which is then picked up on the end of a glass fiber and mounted in the camera.

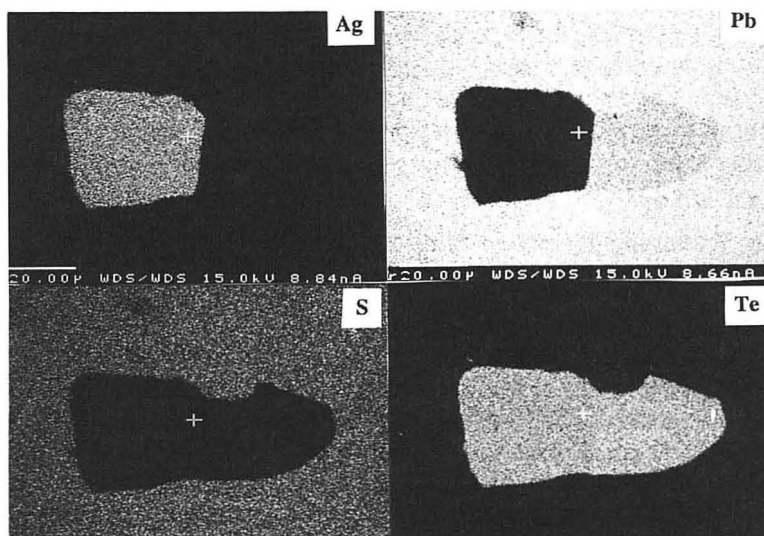
### A3.2 ELECTRON PROBE MICROANALYSIS

The second technique, electron probe microanalysis, also has been described in numerous texts and papers, of which Reed (1975), Heinrich (1981), Harris (1990), and Goldstein et al. (1992) serve as good examples for the mineralogist. A beam of electrons, generated in a potential field of 10–40 kV, strikes the specimen as a spot that may be as small as 1  $\mu\text{m}$  in diameter; the spot can be maintained stationary or can be made to scan rapidly over an area up to several thousand square microns. The electron beam excites the emission of X-rays characteristic of the elements present from the sample, thus enabling the composition of the sample to be determined by analysis of the energies and intensities of the emitted X-rays. A quantitative analysis of a mineral for a particular element is obtained by comparing the intensity (i.e., count rate) of the characteristic X-rays from the sample with the intensity of radiation of the same energy generated by a standard of known composition. Consequently, a complete chemical analysis can be obtained for a spot that may be as little as a few microns in diameter. Concentrations from major elements down to 0.1 wt % can be determined with an accuracy of a fraction of 1%. Most electron probes can rapidly scan areas of several thousand square microns, and the back-scattered electrons can be monitored and used to produce a magnified image (up to 100,000  $\times$ ) of the surface of the specimen. The characteristic X-rays emitted from this area of the surface can also be monitored and used to map out the distribution of elements within and between phases (see Figures A3.1 and A3.2).

A great advantage of the electron probe technique for the ore microscopist is that most instruments directly accept a standard size polished section or polished thin section. The only other preparation usually needed is to apply (by sputtering under vacuum) a thin ( $\sim 200 \text{ \AA}$ ) coat of carbon to the specimen surface in order to conduct away the charge. Therefore, samples can be studied under the ore microscope, and drawings or photographs can be taken of interesting areas that can then be subjected to complete chemical analysis in the electron probe. The electron probe has revolutionized ore mineralogy by enabling the complete chemical analysis of very small grains, including many new minerals (e.g., platinum group metal minerals), the products of laboratory synthesis experiments aimed at establishing phase relations in ore mineral



**FIGURE A3.1** Confirmation of the identity of altaite ( $\text{PbTe}$ ) and hessite ( $\text{Ag}_2\text{Te}$ ) in galena by use of the electron microprobe. Back-scattered electron image in which the heaviest average atomic number phase ( $\text{PbTe}$ ) shows up white, the intermediate average atomic number phase ( $\text{PbS}$ ) shows up gray, and the lightest average atomic number phase ( $\text{Ag}_2\text{Te}$ ) shows up black.



**FIGURE A3.2** Four select element scans showing the distribution of silver ( $\text{Ag}$ ), lead ( $\text{Pb}$ ), sulfur ( $\text{S}$ ), and tellurium ( $\text{Te}$ ) by the intensity of the image (higher concentrations are brighter) in the sample shown in Figure A3.1 (width of field = 170 microns). (We are indebted to Todd Solberg for helping us obtain the microprobe images.)

systems, and optically identifiable minerals that may contain economically important elements in solid solution (e.g., silver within the lattice of tetrahedrite).

A comprehensive treatment of the integration of the ore microscope with the electron microprobe has recently been prepared by Gasparrini (1980).

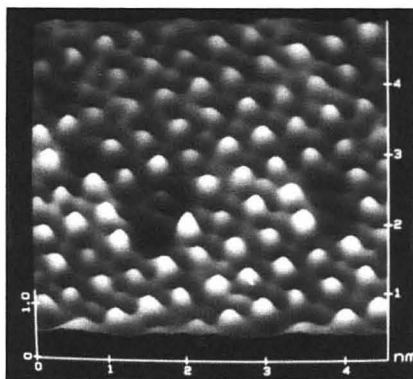
### **A3.2.1 Scanning Electron Microscope (SEM)**

The SEM has become a powerful ancillary technique for the study of ore specimens, and its general applications are discussed in Lloyd (1985) and White (1985). It operates much like an electron microprobe, using a high-energy (usually 10–30 kV) electron beam that is rapidly scanned across the sample. An image is generated by electrons scattered from the surface of the sample; the number of electrons scattered is a function of the average atomic number of each phase. The resulting images closely resemble optical images (Figure 11.9), except that the brightness of the phases varies with atomic number instead of the electronic bonding structure, as does the reflectance of visible light in optical images. SEMs offer a very wide range of magnification but are commonly used to generate images that show intergrowths and structures on the submicron scale that are below these achievable by conventional optical methods. In addition, SEMs are capable of producing excellent images of three-dimensional objects, such as crystals.

Sample preparation is identical to that used for reflected-light microscopy, and, indeed, the same samples must be electrically conducting; hence, most samples require a 50–250 Å thick coating of evaporated carbon (gold, silver, aluminum, or other metals are sometimes used in special applications). This coating does not distort any of the image but can dramatically alter the colors of minerals to the naked eye and under the reflecting microscope (i.e., gold and chalcopyrite become blue, whereas pyrite becomes gray).

### **A3.2.2 Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM)**

STM and AFM are new types of microscopy developed since 1980 that permit examination of surfaces on the atomic scale, hence revealing features that are several orders of magnitude smaller than can be seen by optical or scanning electron microscopy. STM works by moving a sharp metal tip over the surface of a sample that can conduct electricity. When the tip is brought within about 10 Å of the surface, the application of a low voltage allows electrons to be exchanged or “tunneled” across the gap between the tip and the sample. The tunneling electrons are generally exchanged only between the lowest atom of the tip and the closest atom on the surface of the sample. As the tip scans across the surface, the variation in the electric current resulting from tunneling is measured, mapping out the position of each atom as shown in Figure A3.3.



**FIGURE A3.3** Scanning tunneling microscope (STM) image of a (100) cleavage surface of galena. The higher peaks show the locations of sulfur atoms, and the lower peaks are lead atoms. The darker areas represent either defects in the lattice or sites where oxidation has begun to attack the galena. The units on the scales are in nanometers (1 nm = 10 Å). (Image courtesy of M. F. Hochella, taken by C. M. Eggleston.)

AFM instrumentation is similar to that of STM instrumentation, but it employs a very sharp tip that actually touches the sample surface. Instead of relying upon an electrical current, AFM uses an optical laser beam that measures the atomic scale topography as the sharp tipped stylus scans across the sample. It does not reveal actual atoms but clearly shows atomic scale growth steps and other growth or dissolution features. Furthermore, because it does not rely upon electron movement, AFM works as well on insulators as it does on conductors.

STM and AFM are rapidly developing as new techniques that extend the studies initiated by optical microscopy and scanning electron microscopy. Informative discussions on their operation and applications are given in Hansma et al. (1988) and Hochella (1990).

### **A3.3 MICROBEAM METHODS OF TRACE ELEMENT (AND ISOTOPIC) ANALYSIS**

In recent years, new techniques have been developed that enable in situ microanalysis of minerals in polished sections aimed at quantitative trace element analysis and the determination of isotope ratios (Cabri and Chryssoulis, 1990). Of these new techniques, two have been sufficiently developed and applied to ore minerals to justify mentioning here. The proton microprobe (also known as proton-induced X-ray emission, or PIXE) involves directing a (micro) beam of protons (from a small particle accelerator) at the polished surface of the sample, thereby causing the emission of X-rays characteristic of the

elements present in the same way as in the electron probe. The advantage of the proton probe is in the much higher peak-to-background ratio obtained in X-ray emission, enabling measurement of trace elements (at concentrations down to a few parts per million) in individual mineral grains. The ion probe (also known as the technique of secondary ion mass spectrometry, or SIMS) involves bombarding the surface of the sample with a beam of energetic ions that actually sputter material from the surface. This material, in the form of various atoms, ions, and molecules, is directed into a mass spectrometer and analyzed so that relative (or absolute) amounts of species present can be determined. The great sensitivity of this technique enables analysis of trace elements in individual mineral grains. It also enables determination of isotope ratios—data that can help in understanding the processes of formation of the minerals. Both the proton (micro) probe and the ion (micro) probe and their applications in ore mineralogy are discussed in an excellent review by Cabri and Chryssoulis (1990).

### **A3.3.1 Image Analysis**

Image analysis is a generic term for procedures that generally make use of computer processing of photographic or electronic images to quantitatively analyze ores or beneficiated products. The processing relies upon differences in reflectance at specific wavelengths or upon overall gray levels (composite brightness in black-and-white images) to identify grain boundaries and to distinguish between different types of mineral grains. The specimens must be well polished, scratch-free, flat, and uniformly illuminated for good results. Under ideal conditions, image analysis systems can rapidly determine absolute areas of different phases, grain sizes, grain shapes, nearest neighbor relationships, degree of “locking” of phases, and so forth. Poor polish, rounding of grains, variations in composition, or bireflectance can give grains of a single phase a significant range of reflectances (or gray levels). If range of different minerals approach or overlap, image analysis systems will not be able to make accurate determinations. Another problem common in many ores is fracturing of grains as a result of natural or induced stresses. The human eye readily recognizes that a fracture through a grain is secondary, but many image analysis systems will see the fracture as a boundary separating two separate grains. In similar fashion, the characteristic triangular pits in galena may be computed as something other than galena by many systems.

Despite inherent limitations in computer-based image analysis systems, these are finding increasing utility in providing information on ores and mill products. The ability to store large numbers of images and data permits one to examine large numbers of specimens without becoming fatigued. Although the data are gathered from two-dimensional images, they can commonly be converted to give volumetric information. Some image analysis systems also compare or compile chemical compositional data from electron microprobes or SEMs; such an analysis may or may not include optical images. There is no

doubt that image analysis will become more common in the years ahead. Some useful references that describe image analysis techniques are works by Petruk (1989, 1990).

## REFERENCES

- Azaroff, L. V., and Buerger, M. J. (1958). *The Powder Method in X-Ray Crystallography*. McGraw-Hill, New York.
- Cabri, L. J., and Chryssoulis, S. L. (1990). Advanced Methods of Trace Element Microbeam Analysis. In J. L. Jambor and D. J. Vaughan (eds.), *Advanced Microscopic Studies of Ore Minerals*. Min. Assoc. Canada Short Course Hdbk. 17, Ottawa.
- Gasparrini, C. (1980). The role of the ore microscope and electron microprobe in the mining industry. *CIM Bull.* No. 73, 73–85.
- Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, D. C., Romig, A. D., Layman, C. E., Fiori, C., and Lifshin, E. (1992). *Scanning Electron Microscopy and X-Ray Microanalysis*. Plenum Press, New York.
- Hansma, P. K., Elings, V. B., Marti, O., and Bracker, C. E. (1988). Scanning tunneling microscopy and atomic force microscopy: application to biology and technology, *Science*. **242**, 209–216.
- Harris, D. C. (1990). Electron Microprobe Analysis. In J. L. Jambor and D. J. Vaughan (eds.), *Advanced Microscopic Studies of Ore Minerals*. Min. Assoc. Canada, Short Course Hdbk. 17, Ottawa.
- Heinrich, K. F. J. (1981). *Electron Beam X-Ray Microanalysis*. Van Nostrand Reinhold, New York.
- Hochella, M. F. (1990). Atomic Structure, Microtopography, Composition and Reactivity of Mineral Surfaces. In M. F. Hochella and A. F. White (eds.), *Mineral-Water Interface Geochemistry, Reviews in Mineralogy*. Mineral. Soc. America. pp. 87–132, Washington D.C.
- Lloyd, G. (1985). Review of Instrumentation, Techniques, and Applications of SEM in Mineralogy. In J. C. White (ed.), *Applications of Electron Microscopy in the Earth Sciences*. Mineral. Assoc. Canada Short Course Hdbk. 11, pp. 151–188, Ottawa.
- Nuffield, E. W. (1966). *X-Ray Diffraction Methods*. Wiley, New York.
- Petruk, W., ed. (1989). *Short Course on Image Analysis Applied to Mineral and Earth Sciences*. Mineral Assoc. Canada, Short Course Hdbk. 16, Ottawa.
- Petruk, W. (1990). Determining Mineralogical Characteristics by Image Analysis. In J. L. Jambor and D. J. Vaughan (eds.), *Advanced Microscopic Studies of Ore Minerals*. Mineral Assoc. Canada Short Course Hdbk. 17, pp. 409–425, Ottawa.
- Reed, S. J. B. (1975). *Electron Microprobe Analysis*. Cambridge University Press, Cambridge, England.
- Smith, D. G. W., ed. (1976). *Microbeam Techniques*. Min. Assoc. Canada Short Course Hdbk. 1, Toronto.
- White, J. C., ed. (1985). *Application of Electron Microscopy in the Earth Sciences*. Mineral. Assoc. Canada, Short Course Hdbk. 11, Ottawa.
- Zussman, J. (1977) X-Ray Diffraction. In J. Zussman (ed.), *Physical Methods in Determinative Mineralogy*. Academic, New York.