DOWN TO THE NANOSCALE: STRUCTURAL AND CHEMICAL PROPERTIES OF MINERALS AS OBTAINED FROM TEM, STEM, EDX AND EELS

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The transmission electron microscope (TEM) has become an integral part of up-to-date mineralogical research. In a single instrument multiple types of data and observations (imaging, diffraction, spectroscopy) can be obtained on the same mineral grain down to the nanoscale. Analytical TEM provides important information on the chemical composition and real structures of minerals (including lattice defects). These data allow us, for example, to understand how minerals transform and deform and how chemical elements are incorporated (coordination, site symmetry, valence state) and partitioned between minerals. The various TEM methods available to extract this information are:

<u>(1) Conventional (CTEM) and high resolution (HRTEM) imaging</u>
Imaging techniques are used to observe the microstructures of mineral aggregates and to characterize the periodicities and imperfections (0-, 1-, and 2-dimensional lattice defects) in mineral structures. TEM imaging is in principle a two-stage process that involves *(a)* the diffraction of the incident electron beam by the specimen and *(b)* the recombination of the transmitted and diffracted beams to form an image. In conventional TEM, a significant number of diffracted beams is excluded from the image formation process using an objective aperture. This causes a strong amplitude contrast that can be used to image lattice defects. On the contrary, HRTEM involves the recombination of many beams and produces an image containing primarily information on the phases of the diffracted beams. To a first approximation, such *"phase contrast"* images reveal the electrostatic potential of a specimen, which, in turn, is a direct image of the structure.

<u>(2) Electron diffraction techniques (SAED and CBED)</u>
Electron diffraction patterns represent two-dimensional sections through reciprocal space. The objective lens collects the diffracted beams and focuses them into the back focal plane, the plane of the diffraction pattern. In the selected area electron diffraction (SAED) technique, the specimen is illuminated with a parallel beam, producing discrete spots (single crystal) or rings (polycrystalline aggregate) in reciprocal space. On the other hand, convergent beam electron diffraction (CBED) involves the illumination of the specimen with a highly convergent beam, producing diffraction discs in the back focal plane.
Electron diffraction provides valuable information on the symmetry, interplanar spacings, and lattice constants of crystals. Electron diffraction techniques are important for the identification of minerals and the determination of the crystallographic orientation and character of lattice defects as well as the orientation relationship between coexisting phases.

(3) Spectroscopic techniques (EDX and EELS)

There are basically two types of spectroscopic techniques used on a modern TEM: *(a)* energy dispersive X-ray (EDX) and *(b)* electron energy loss spectroscopy (EELS). The EDX technique analyzes the X-ray photons generated by the interaction of the incoming electrons with the specimen atoms. The intensities of X-ray peaks are influenced by instrumental and geometrical factors as well as by absorption. The correction of X-ray absorption is particularly important for the quantification of light elements such as oxygen. Therefore, the quantification of mineral analyses is nowadays usually based on the so-called Van Cappellen method, which assumes that the sum of all anions and cations times their respective valence states must balance. The advantage of X-ray microanalysis on a TEM is the high lateral resolution, which allows us to measure even very short sub-μm diffusion profiles between adjacent minerals that are not accessible by any other technique.

Electron energy loss spectroscopy (EELS) is the analysis of the energies of transmitted electrons that have inelastically interacted with the specimen. There are a number of possible interactions, such as interactions with valence (plasmon loss) or inner-shell electrons (core loss). The inelastic collisions of electrons tell us a tremendous amount about the electronic structure of the specimen atoms. In mineralogical applications, the core losses are the most interesting signals, providing useful information on bonding type, coordination and valence states of elements.

The lectures will comprise various exercises demonstrating how to index diffraction patterns and planar defects and how to determine the Burgers vectors of dislocations from amplitude contrast images. The course will also include practical examples on the quantification of EDX and EELS spectra.

Literature

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