Mössbauer effect and TEM in mineralogy

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Mössbauer effect (ME) provides useful information on oxidation state, co-ordination number, co-ordination state, site occupancies, and magnetic properties of Fe-bearing phases. The information gained by ME together with the information provided by other conventional techniques is used to extract temperature, pressure, and kinetics of rock-forming processes. Nevertheless, ME requires that the phases studied are homogeneous over an extremely large volume and that Fe is a major component of the system. Transmission electron microscopy (TEM), on the other hand, provides similar information over a very small volume for a system of any component. However, present TEM spectrometers do not provide sufficient resolution to detect the mixed oxidation state. A complete characterisation of phases in rocks requires, therefore, that conventional techniques be combined with TEM.

1. Introduction

Rocks are chemical systems composed of one or more phases. To understand the temperature and pressure histories of rocks, it is necessary to characterise the phases fully and correctly. For this, we need to determine the compositions of the phases and the site occupancies of their constituent elements. Electron-induced X-ray microanalysis, neutron diffraction, and X-ray diffraction (XRD) are the common experimental techniques used. Site occupancy refinement using X-ray diffraction is, however, limited to elements with significant difference in electron scattering amplitudes. Moreover, the crystals studied must be chemically homogeneous over large volumes. Mössbauer effect (ME) is also useful in studying the oxidation ratio, co-ordination number, co-ordination state, and magnetic properties of iron in rock-forming minerals. However, the determination of site occupancies is by far the most significant application of ME in geology. Mössbauer effect is, nevertheless, a bulk spectroscopy, and the information gathered is averaged over many unit cells. Moreover, since Fe is the only important Mössbauer atom in minerals, the application of ME in mineralogy is limited.

Transmission electron microscopy, TEM, has shown that chemical and structural perturbations are widespread defects in rock-forming minerals. The common ones are exsolution, chain-width disorder, stacking faults, clustering, and inclusions of foreign crystallites. These defects are beyond the resolution of conventional techniques,
including Mössbauer effect and X-ray diffraction. A complete characterisation of the phases present in rocks can be realised, therefore, only by combining conventional techniques with TEM. Moreover, TEM can be used independently to determine site occupancies and the oxidation state of atoms in minerals by electron channelling (ALCHEMI) and electron energy-loss spectroscopy (EELS), respectively. These properties make TEM a useful tool for characterising mineral phases.

The aim of this paper is to compare and contrast the application of ME and TEM in mineralogy. I will try to identify the strength and weakness of one over the other and explore the potentials of combining the two.

2. Determination of site occupancies: ME versus TEM

The determination of site occupancies in minerals is of considerable interest for petrologists and mineral spectroscopists. The amount of atomic ordering in minerals supplies information on the temperature and pressure of rock-forming processes. The commonly used techniques for site occupancy studies are X-ray and neutron diffraction. For Fe-bearing minerals, however, ME is a cheap and useful alternative. The principle of deriving occupancies from peak area ratios and microprobe data is discussed in detail by Bancroft [1] and is summarised by Hawthorne [2]. A brief survey on the application of ME in the determination of site occupancies in some of the common rock-forming minerals is presented by Hawthorne [2].

However, for valid determinations of site occupancies using ME, valid site assignments of the ME doublets are essential. In those cases where the ME spectra are well resolved, spectral interpretation and site assignments are straightforward, while in those cases where there are spectral overlaps, site assignments depend on the structural model assumed and the constraints adopted. For example, in the ortho-amphiboles the Mössbauer spectrum of anthophyllite shows pairs of well-resolved doublets, while the corresponding spectrum of gedrite shows spectral overlap that makes site assignments difficult [3,4].

The technique employed for site determination in the TEM is known as electron channelling or ALCHEMI (atom location by channelling enhanced microanalysis). In ALCHEMI, an orientation is chosen such that: (i) the sites of interest are located on alternating planes; (ii) there is ample difference in projected potential between the planes; and (iii) at least one atom, serving as an internal standard, is confined to just one of the planes. Based on computer simulations, Smyth and MacCormick [5] have surveyed the minerals and the orientations that meet these requirements. The theory and applications of ALCHEMI have been reviewed, among others, by Spence [6] and by Buseck and Self [7]. A practical guide to ALCHEMI is provided by Otten [8]. Olivine has a very simple crystal structure and it is one of the first minerals studied by ALCHEMI [9]. Here I will, using olivine as an example, briefly explain the working principle of ALCHEMI.

Electron channelling is based on the modulation of the electron beam current within a unit cell. The modulation is more pronounced where there is strong diffraction.