Possibilities of Mössbauer Spectrometry in Geology and in Environmental Science

MARCEL MIGLIERINI

Department of Nuclear Physics and Technology Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia, e-mail: bruno@elf.stuba.sk

Abstract. Basic principles of Mössbauer spectrometry are briefly summarised with special emphasis put on hyperfine interactions and their relation with spectral parameters. Qualitative and quantitative analysis enables determination of crystallographic phases present in the sample and determination of stochiometry, respectively. Using the latter, oxidation states of iron via determination of Fe(II)/Fe(III) ratio can be obtained. Unique features of Mössbauer effect technique which provide simultaneous information on structure and magnetic state of the resonant atoms are effectively applied for the usage of this method in geology and also in environmental science. Some illustrative examples are discussed to more details. An importance of Mössbauer spectrometry is underlined by its involvement in extraterrestrial missions.

Keywords: Mössbauer spectrometry, hyperfine interactions, phase composition

Mössbauer spectrometry

Mössbauer spectrometry provides simultaneous information about structural arrangement of the resonant atoms and their magnetic states. Both can be unveiled from deviations in the positions of nuclear energy levels which sensitively reflect influence of hyperfine interactions. The latter are governed by location of the resonant atoms in particular crystalline sites, their oxidation state, coordination number, site symmetry, etc. The type and the number of the nearest neighbours should they be constitution element, substitutional ligands or even impurities and/or lattice defects play a crucial role. As a result of the above mentioned effects, electric and magnetic moments are present and they cause splitting of nuclear energy levels. As demonstrated in Fig. 1, characteristic types of Mössbauer spectra and their respective spectral parameters are observed which can be directly correlated with particular hyperfine interactions.

Mössbauer spectrum parameters of crystalline systems are discrete values. They can be, similar as fingerprints, unambiguously assigned to various structural positions of the resonant atoms. Positions of lines provide information on the intensity of hyperfine magnetic field B or on the tensor of electric field (derived from the spectral parameters called quadrupole splitting – D) at the nuclei as well as on the density of electron cloud inside the nucleus (isomer shift – d). Linewidths are proportional to structure (defects, ordering) and line intensities (line areas) give the orientation of the net magnetization. Line area of the particular spectral component is directly proportional to the relative number of resonant atoms in that particular structural positions which grants a quantitative analysis or determination of stochiometry of the investigated sample.

Mössbauer Spectrometry in Geology

At present, about 47 elements featuring nearly 110 transitions can be used for the observation of the Mössbauer effect and, in turn, for spectroscopic purposes. However, almost 65% of scientific papers in this field are devoted to the usage of the isotope of iron ^{57}Fe (Mössbauer Data Center, 2003). Because iron is widely abundant element in geological species, too, application of Mössbauer spectrometry in geology is straightforward.

The diagnostic potential of Mössbauer spectrometry can be effectively utilised in the determination of magnetic and non-magnetic lattices. Typical materials in this respect are magnetic oxides and magnetic fractions of minerals, intermetallic compounds and other materials interesting from the technological viewpoint. Especially in magnetically ordered minerals, Mössbauer parameters can be ascertained for each sublattice individually. Subsequently, individual moments, magnetic ordering temperature as well as magnetic structure can be identified (Lipka, 1999). Typical example is shown in Fig. 2 where a transmission Mössbauer spectrum of magnetite is displayed. It can be decomposed into two subspectra that belong to atoms positioned in tetrahedral and octahedral crystallographic sites. A comparison with a Mössbauer spectrum of metallic iron points out significant quantitative differences between these two examples as far as the hyperfine field value is concerned even though the same type of hyperfine interactions (magnetic dipole) applies.

Mössbauer spectrometry provides a simple means of quantitative measurement of the distribution of iron among its oxidation states, e. g. Fe(II)/Fe(III) ratio, based on the magnitude of isomer shift and quadrupole splitting. At the same time, qualitative analysis is also possi-

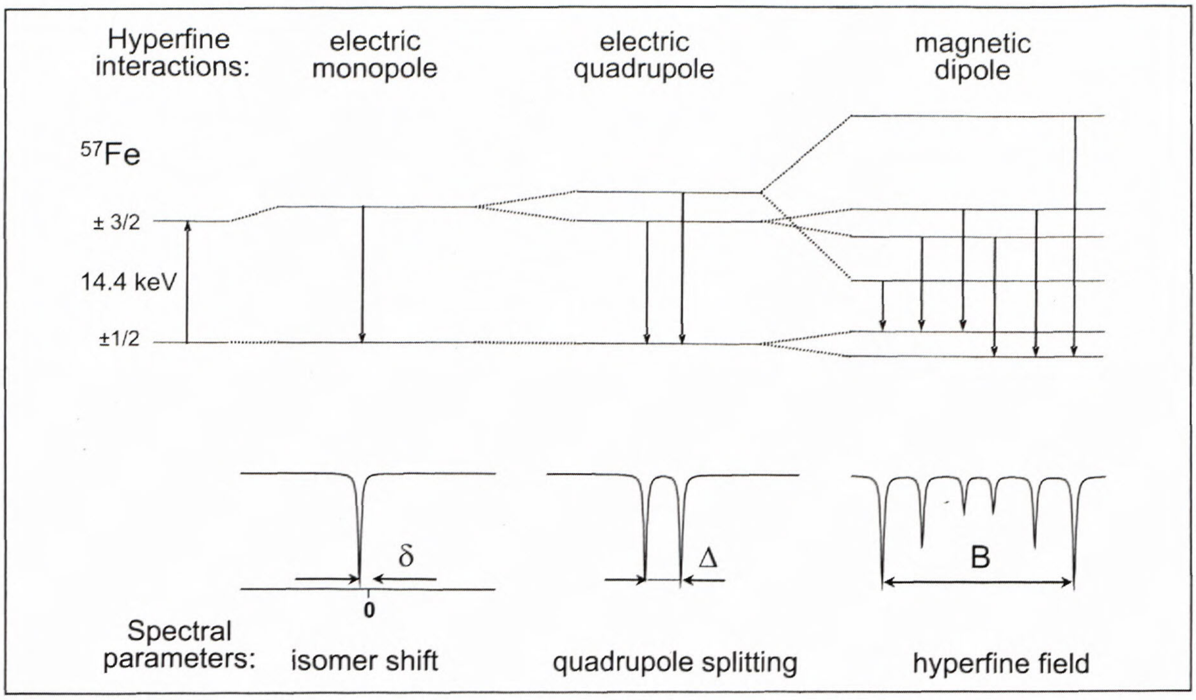

Fig. 1. Hyperfine interactions for ^{57}Fe nuclei and their influence on the shape of Mössbauer spectra.

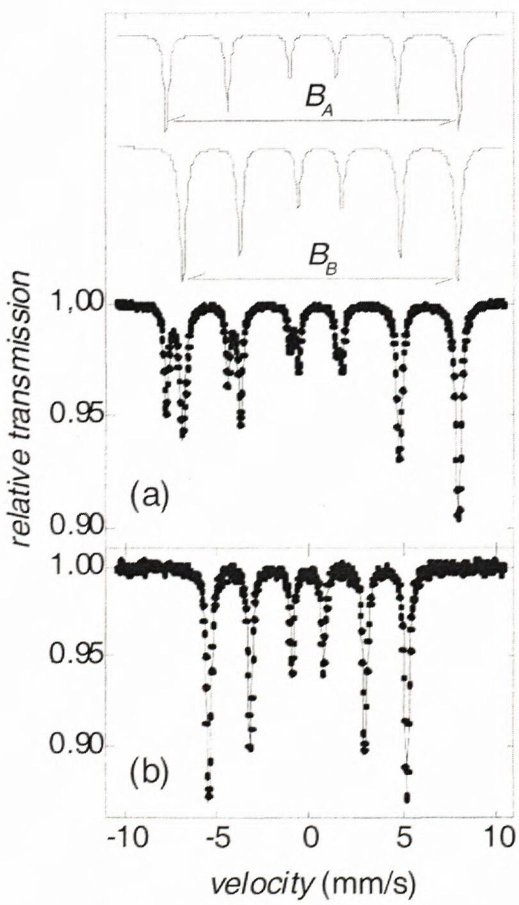

Fig. 2. Room temperature transmission ^{57}Fe Mössbauer spectra of (a) magnetite (Fe_3O_4) decomposed into spectral components: A – tetrahedral (B_A = 49.4T) and B – octahedral (B_B = 45.8T) sites of iron ions; (b) natural iron (B = 33.1 T).

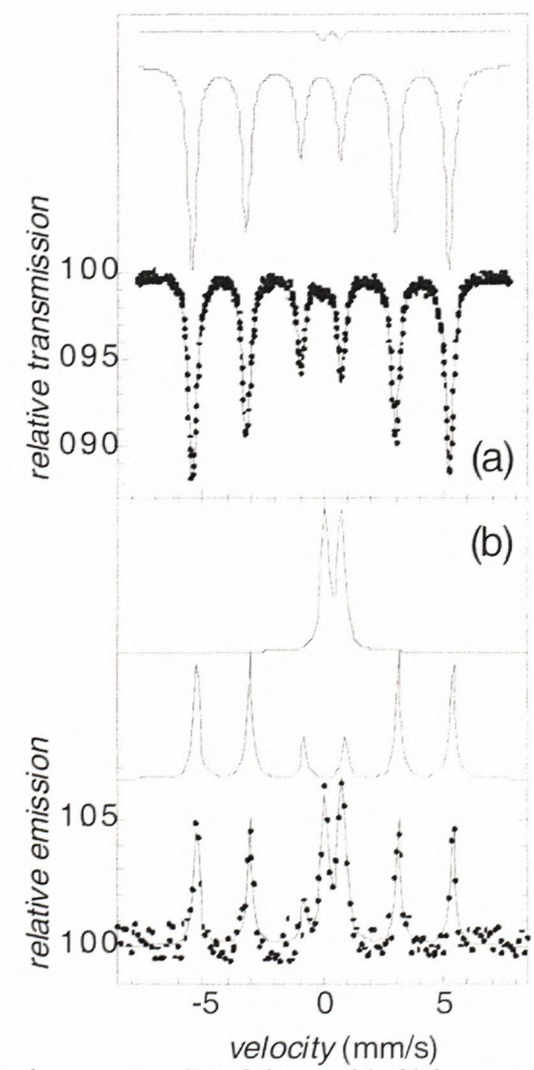

Fig. 3. Room temperature transmission (a) and emission (b) ^{57}Fe Mössbauer spectra of iron foil exposed for 21 days to ambient atmosphere in industrial urban area including spectral components (see text).

Mössbauer Spectrometry in Environmental Science

Crystalline α-Fe is a basic absorber for ^{57}Fe Mössbauer spectrometry. Its hyperfine parameters are well known and some of them are used to calibrate the experimental apparatus. Consequently, such material can be employed for environmental studies. Changes in bulk and to higher extent those of surface sensitively reflect the effects of environmental conditions.

Example of air monitoring with the help of Mössbauer spectroscopy is documented in Fig. 3. Calibration α-Fe foil (thickness of 25 μm) was exposed for 21 days to ambient atmosphere on a territory of a huge urban agglomeration. As a result, iron oxides were created.

Classical transmission geometry experiment showed only minor perturbation of the resulting Mössbauer spectrum (Fig. 3a) which was collected from a sample positioned in a vicinity of an industrial plant. It consists of two components: sextet of Lorentzian lines attributed to α-Fe substrate and a doublet which represents iron oxides induced by atmospheric conditions. Contribution of the latter is about 6%. Then we have applied conversion electron Mössbauer spectrometry (Miglierini and Seberíni, 2000) which is sensitive to resonant atoms located in surface regions to the depth of ca. 100 nm. Emission Mössbauer spectrum of conversion electrons in Fig. 3b unveiled that surface regions consist to almost 38% of oxides. Sextet of spectral lines belongs to the foil itself, i. e. α-Fe crystalline substrate.

Evaluation of samples placed in industry free areas disclosed lower amount of oxides on their surface which suggests smaller impact of atmospheric conditions on their formation.

Conclusions

Iron is one of key elements in the evolution of our planet. The identification and determination of iron bearing minerals, their weathering products, Fe(II)/Fe(III) ratio, and properties of magnetic phases can contribute to the understanding of chemical and physical processes in geology and environmental science. In this respect, Mössbauer spectrometry contributes significantly. Its unchangeable role is documented by the fact that Mössbauer spectrometers were mounted on board of space rovers which were launched in June 2003 for Mars missions (Mars exploration rover, 2003). It is foreseen that iron-bearing minerals such as carbonates, phyllosilicates, hydroxyoxides, phosphates, oxides, silicates, sulphides, sulphates, etc. including those that are magnetically ordered could be identified. The obtained data would help in the characterisation of the present state of Martian surface. In this way the possibilities of Mössbauer spectrometry in geology are extended also to extraterrestrial applications.

Acknowledgement

Financial contribution of the grant KEGA 3/100503 is acknowledged.

References

Web page of Mössbauer Effect Data Center: http://www.unca.edu/-medc/Statistics.html.

Lipka, J.: *Mössbauer Spectroscopy in Mineralogy and Geology* in: Mössbauer Spectroscopy in Materials Science, eds. M. Miglierini and D. Petridis, Kluwer Academic Publishers, 1999, The Netherlands, p. 97-106.

Mars exploration rover web page: http://athena.cornell.edu/the mission/-ins moss.html.

Miglierini, M. & Seberíni, M.: *Conversion Electrons – A Way to Study Surface Crystallization*, in: Proc. 6th Int. Workshop on Applied Physics of Condensed Matter, APCOM 2000, Kočovce, Slovakia, 19.-21.6.2000, p. 84-87.