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Geochemical Instrumentation and Analysis

Mössbauer Spectroscopy

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What is Mössbauer Spectroscopy

The technique of Mössbauer spectroscopy is widely used in mineralogy to examine the valence state of iron, which is found in nature as Fe^0 (metal), Fe^{2+} , and Fe^{3+} , as well as the type of coordination polyhedron occupied by iron atoms (trigonal, tetrahedral, octahedral, etc.). It is sometimes used to determine redox ratios in glasses and (less successfully) in rocks. Mössbauer spectroscopy is also used to assist in the identification of Fe oxide phases on the basis of their magnetic properties.

Fundamental Principles of Mössbauer Spectroscopy

The Mössbauer effect as generally applied to the study of minerals relies on the fact that ^{57}Fe , which is a decay product of ^{57}Co , is unstable. ^{57}Fe decays by giving off a gamma ray (γ -ray), along with other types of energy. Figure 1 shows the nuclear decay scheme for $^{57}\text{Co} \rightarrow ^{57}\text{Fe}$ and various backscattering processes for ^{57}Fe that can follow resonant absorption of an incident gamma photon, modified from DeGrave et al. (2005) and Dyar et al. (2006). If a nucleus gives off radiation or any other form of energy (in this case, in the form of a γ -ray), the nucleus must recoil (or move) with an equal and opposite momentum to preserve its energy (E), in the same way that a gun (by analogy, the nucleus) recoils when a bullet (the γ -ray) is fired out of it. We describe this general case in terms of energy by saying that:

$$E_{\gamma\text{-ray emission}} = E_{\text{transition}} - E_R$$

where

$E_{\gamma\text{-ray emission}}$ = the energy of the emitted γ -ray

$E_{\text{transition}}$ = the energy of the nuclear transition

E_R = the energy of the recoil.

Figure 2 shows a schematic of the vibrational energy levels in a solid. On the left, the recoil energy E_R of an emitted gamma photon is less than what is needed to reach the next higher energy level, so that excitation of a vibrational mode has low probability. The probability that no excitation will occur is given the symbol f , which represents the fraction of recoil-free events. A gamma ray would be emitted without losing energy to the solid, in what is called a zero-phonon transition. In other words, sometimes the nucleus absorbs the energy of the γ -ray and it doesn't recoil (instead, the entire structure, rather than just the nucleus, absorbs the energy). The variable f indicates the probability of this happening. This process of recoil-less emission forms the basis for Mössbauer spectroscopy. On the right, E_R is significantly greater in energy than the lowest excitation energy of the solid, which is $E_{n+1} - E_n$. Absorption of the recoil energy, E_R , by the solid thus becomes probable, and the photon emerges with energy reduced by E_R and with Doppler broadening. In the figure, ω represents frequency, and \hbar is Planck's constant divided by 2π , and This figure is adapted from May (1971) and Dyar et al. (2006).

The Mössbauer effect occurs because in solids, the value of f is high enough that recoil-free absorption is possible. Thus an atom of ^{57}Co can decay to ^{57}Fe , which gives off a γ -ray, and may be absorbed without recoil by a nearby ^{57}Fe , which happens to have just the right splitting between the energy levels in its nucleus to absorb it. This scenario will only happen if the decaying Co atom is surrounded by the same atoms as the absorbing Fe. If the receiving Fe atoms are in a different matrix (say, in a mineral) than in the emitter, then no absorption can occur.

When source and absorber atoms are in different local environments, their nuclear energy levels are different (Figure 3). At its simplest (blue), this appears in the transmission spectrum as a shift of the minimum away from zero velocity; this shift is generally called isomer shift (IS). The 1/2 and 3/2 labels represent the nuclear spin, or intrinsic angular momentum, quantum numbers, I . Interaction of the nuclear quadrupole moment with the electric field gradient leads to splitting of the nuclear energy levels (red). For ^{57}Fe , this causes individual peaks in the transmission spectrum to split into doublets (red) having a quadrupole splitting of QS. When a magnetic field is present at the nucleus, Zeeman splitting takes place, yielding a sextet

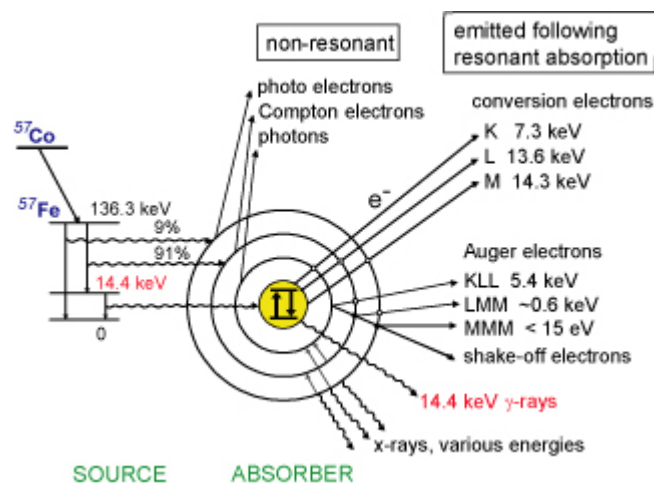


Figure 1. [Details](#)

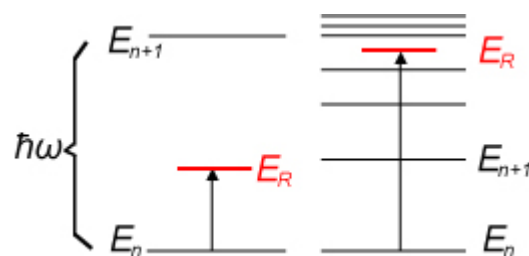


Figure 2. [Details](#)

pattern (green); in the simplest case, the areas of the lines vary in the ratio of 3:2:1:1:2:3. For the spectrum shown, the outer lines have reduced intensity because of saturation effects. Two additional possible transitions shown in gray at lower right ($m_I = -1/2$ to $+3/2$ and $m_I = +1/2$ to $-3/2$) do not occur due to the selection rule, $|\Delta m_I| \leq 1$. Note that the lengths of the transition arrows have been greatly shortened to allow the splittings to be seen clearly. This figure is adapted from Dyar et al. (2006).

So Mössbauer spectra are described using three parameters: isomer shift (δ), which arises from the difference in s electron density between the source and the absorber, quadrupole splitting (Δ which is a shift in nuclear energy levels that is induced by an electric field gradient caused by nearby electrons, and hyperfine splitting (for magnetic materials only). Graphically, quadrupole splitting is the separation between the two component peaks of a doublet, and isomer shift is the difference between the midpoint of the doublet and zero on the velocity scale (Figure 3).

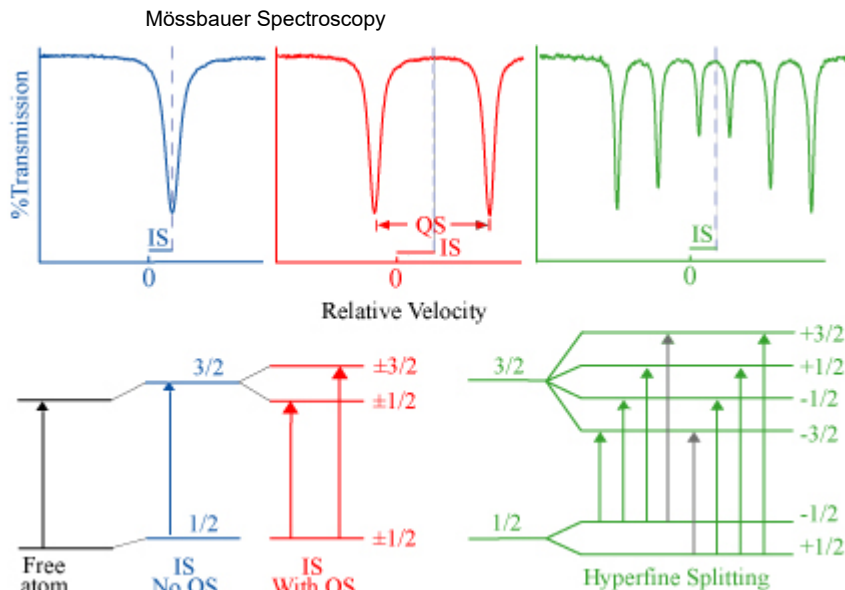


Figure 3. [Details](#)

Mössbauer parameters are temperature-sensitive, and this characteristic is sometimes exploited by using lower temperatures to improve peak resolution and induce interesting magnetic phenomena.

If the electrons around the Fe atom create a magnetic field, as in the case of magnetite, then the energy levels in the Fe nucleus will split to allow six possible nuclear transitions, and a sextet (six-peak) spectrum results. The positions of the peaks in the sextet defines what is called the hyperfine splitting (Hint or BHF, depending on the units used) of the nuclear energy levels.

Iron atoms in different local environments and those having different oxidation states absorb at different, diagnostic energies. A typical Mössbauer spectrum thus consists of sets of peaks (usually doublets and sextets), with each set corresponding to an iron nucleus in a specific environment in the sample (an Fe nuclear site). Different sets of peaks appear depending on what the Fe nucleus "sees" in its environment. The nuclear environment depends on a number of factors including the number of electrons (Fe^0 , Fe^{2+} , Fe^{3+}), the number of coordinating anions, the symmetry of the site, and the presence/absence of magnetic ordering (which may be temperature-dependent). Thus the spectrum of a given mineral may consist of a superposition of doublets and sextets.

The combination of isomer shift and quadrupole splitting parameters (along with the hyperfine field, in the case of magnetically ordered phases) is usually sufficient to identify the valence state and site occupancy of Fe in a given site and individual mineral (Figure 4). In minerals, these ranges have largely been determined empirically from Mössbauer spectra measured with use of spectrum-fitting routines commonly available to the geological community. Exact values of Mössbauer parameters are difficult to predict from theory because long-range interactions in complicated mineral structures are difficult to anticipate.

As seen in Figure 4, Fe atoms in minerals are predictably found in coordination polyhedra of appropriate size based on radius ratios. The top half of Figure 4 plots the isomer shift and quadrupole splitting of several minerals whose iron valence state and coordination number are independently known (usually from single crystal X-ray diffraction), and the bottom of the figure shows the resultant groupings. Fe^{3+} occurs primarily in 4- or 6-coordination with oxygen, while Fe^{2+} may be rarely 4- or 5- coordinated, commonly 6-coordinated, and occasionally 8-coordinated with oxygen. Fe in 4-fold coordination with sulfur has subtly different parameters due to the effects of covalent bonding. Variations in Mössbauer parameters that are characteristic of each type of coordination polyhedron can be related to polyhedral site distortion; a thoughtful discussion of this topic can be found in Burns & Solberg (1988).

Mössbauer Spectroscopy Instrumentation - How Does It Work?

The basic elements of a Mössbauer spectrometer are a source, sample, detector, and a drive to move the source or absorber. Most commonly, this is done by moving the source toward and away from the sample, while varying velocity linearly with time. For example, for ^{57}Fe , moving the source at

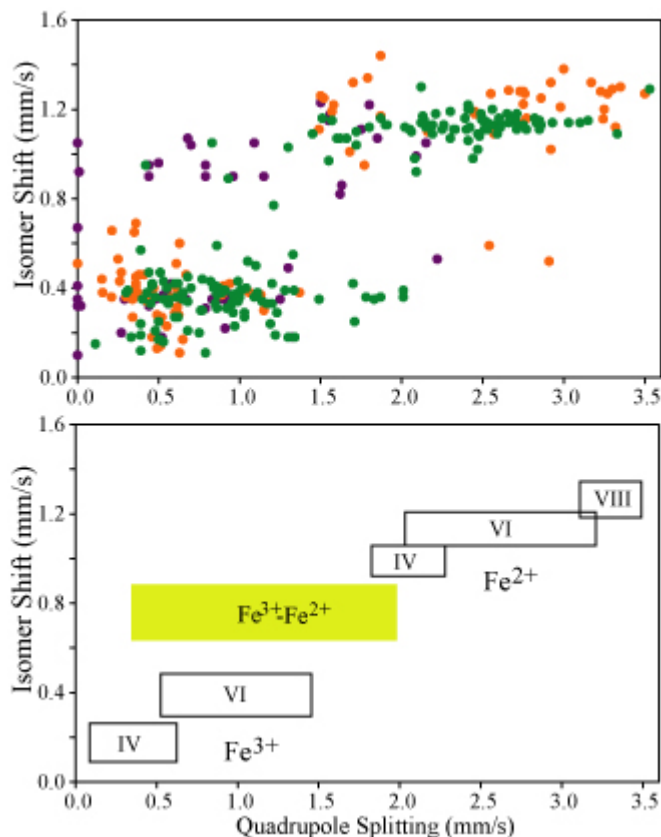


Figure 4. [Details](#)

a velocity of 1 mm/sec toward the sample increases the energy of the emitted photons by about ten natural linewidths. For simplicity, "mm/sec" is the conventional "energy" unit in Mössbauer spectroscopy. It is also possible to leave the source stationary and oscillate the sample, as is done with synchrotron Mössbauer. The location of the detector relative to the source and the sample defines the geometry of the experiment (Figure 5); most commonly, either transmission or backscatter modes are used.

Applications

The combination of isomer shift and quadrupole splitting (along with the hyperfine field, in the case of magnetic phases) is used to identify the valence state and site occupancy of Fe in a given site and individual mineral (Figure 4). If the phase is magnetically ordered, additional information in the form of a value for the magnetic field (usually given in Teslas) can help with identification of some phases.

In some cases, Mössbauer spectrometers are also used to identify minerals. This application is limited, however, by the fact that many different minerals can have site geometries that are the same, such that their Mössbauer spectra and the resultant peak parameters will also be the same. For example, the spectra of amphibole and pyroxene group minerals are all very similar, so you could not tell these minerals apart by their Mössbauer spectra alone!

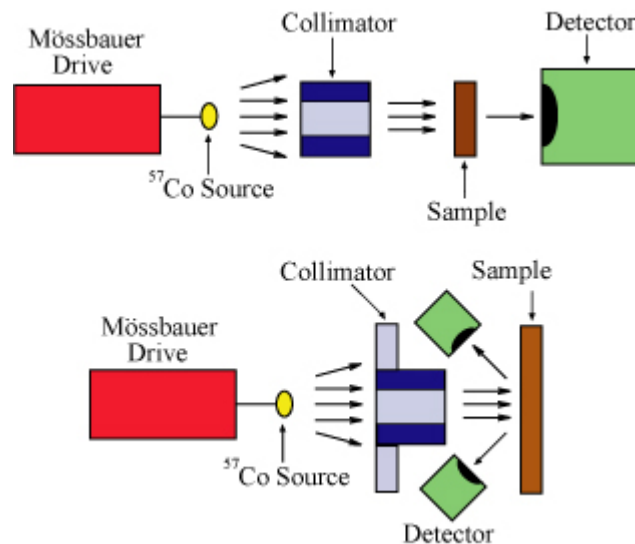


Figure 5. [Details](#)

Strengths and Limitations of Mössbauer Spectroscopy?

Strengths

Along with wet chemistry, Mössbauer spectroscopy remains the "gold standard" for quantitative determination of the valence state of iron in minerals and identification of various iron oxides. It is also well-suited for determination of the coordination number of Fe atoms.

Limitations

The biggest limitation of the Mössbauer is that it is inherently a bulk technique; it uses powders spread thinly across an absorber to get optimal experimental conditions. In recent years, improvements in electronics and detectors have made it possible to run very small samples (1-5 mg). Another approach to this problem is the Mössbauer milliprobe developed by Catherine McCammon at Bayreuth (e.g. McCammon, 1994). This modification, which uses a lead plate to restrict gamma rays to a small diameter (~100 μm), can be used to study single grains in thin sections or single crystals.

The vast majority of rock-forming minerals on Earth contain Fe^{2+} in octahedral coordination, and thus have very similar Mössbauer parameters. For example, pyroxene, amphibole, and mica spectra are all nearly indistinguishable. Furthermore, most minerals exhibit a range of Mössbauer parameters as a function of cation substitution. Finally, the parameters vary as a function of temperature, and the magnitude of that variation is distinctive to each mineral composition. For these reasons, Mössbauer spectroscopy is not ideally suited to mineral identification (except for iron oxides, where magnetic properties can be extremely diagnostic) and is typically not used for this purpose (though it has been pressed into such service in extraterrestrial applications).

User's Guide - Sample Collection and Preparation

Sample preparation for Mössbauer spectroscopy is relatively simple. The sample to be analyzed is powdered and spread across a sample holder with a diameter equal to that of the window in the detector. The amount of sample used affects the resultant spectrum. If too little sample is used, then some γ -rays will never encounter an Fe atom, and therefore have no chance to experience recoil-less emission. Use of too much sample can affect the area, intensity, width, and detailed shape of the Mössbauer lines. If the chemical composition of the material is known before the experiment, then the optimal amount of sample for any given experimental geometry can be calculated.

In most laboratories, samples are mixed with some inert material such as sucrose or graphite to assist in spreading the sample evenly across the diameter of the sample holder. The sample is then held in place with something thin and non-absorbant to γ -rays such as cellophane or kapton tape.

Data Collection, Results and Presentation

Techniques for processing Mössbauer data are complex and variable. There are many Mössbauer spectral analysis programs used to interpret the spectra of geologic (and other) materials. Mössbauer spectra of minerals frequently exhibit highly overlapping peaks, and under these conditions the particular fitting techniques and model assumptions used can make a difference in how the spectra are interpreted. Typically, members of a research group will use only one of these spectral analysis programs, and differences in interpretation that might arise from the use of different programs are therefore virtually unknown. In addition, there are many physical models that have been applied to interpret Mössbauer spectra, and there have been very few published comparisons of any of these models.

Software for analysis of Mössbauer spectra uses a variety of different physical models to generate model spectra with which to compare the measured spectra, and different fitting algorithms to analyze the data. It is important to assume a theoretically reasonable model when fitting Mössbauer spectra because it is possible, based on the data alone, to fit spectra to an unphysical model and still get superficially reasonable chi-squared values. Three different line shapes are commonly employed in modeling of Mössbauer spectra (Figure 6).

- Lorentzian (Cauchy) line shapes, used to describe spectral lines resulting from broadened resonance and other phenomena, have been used since the technique was first developed. This line shape gives a good approximation of line shapes in spectra of paramagnetic materials where all of the Fe nuclei are in identical electronic environments. It is less useful when variations in the geometry of the coordination polyhedra and variable distance between the Fe atom and nearest oxygens and next nearest cations occur—as is the case in most minerals.
- Beginning in the 1970's, many Mössbauer routines began to address the variations in coordination polyhedra around the Fe nucleus by adding a Gaussian component to the Lorentzian line shape. The resultant hybrid line shape, which is a Gaussian distribution of Lorentzian line shapes, is called a Voigt line shape, and is generally approximated by a linear combination of the two line shapes that is called a pseudo-Voigt function (Figure 6).
- Quadrupole splitting distributions (QSDs) are a further evolution in modeling Mossbauer spectra of minerals in which there are poorly-resolved quadrupole pairs, as is certainly the case in phyllosilicate spectra. The QSDs model the local distortions and atomic disorder surrounding the Fe atoms, rather than simply reflecting the ideal point symmetries of the relevant sites. The QSD method performs better than Lorentzian fits in a number of ways. Fits with Lorentzian doublets tend to overestimate the spectral backgrounds, put large wings or tails on the main absorption peaks, and give unreasonably large linewidths.

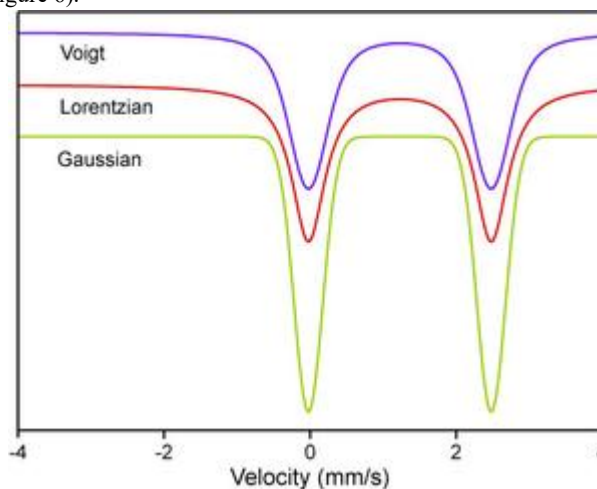


Figure 6. [Details](#)

Error analysis varies from laboratory to laboratory. In general, areas of doublets are quoted to no better than one significant figure after the decimal. Values of isomer shift and quadrupole splitting are usually ± 0.02 mm/s, and hyperfine fields are highly variable. Mössbauer spectroscopy can generally detect features down to roughly 1% of the total Fe. The technique usually is not used for samples containing less than 0.1 wt% FeO.

One final and fundamental constraint on geological applications of Mössbauer results must be mentioned because it is frequently misunderstood. ^{57}Fe Mössbauer spectroscopy can determine only the relative amounts of iron in various types of sites and valence states. It cannot determine the total number of Fe atoms that are present in a material (i.e., relative to the other atoms present) because the presence of other elements has no effect on the Mössbauer spectrum except as they alter the Fe environment and reduce the overall intensity of the spectrum, but not its dependence on velocity. It should be emphasized, therefore, that Mössbauer spectroscopy is a tool to investigate the nature and relative contents of Fe-bearing minerals in a sample. It provides no information on minerals that do not contain Fe in their structures.

Literature

The following literature can be used to further explore Mössbauer Spectroscopy

Mössbauer spectroscopy is a topic that is frequently covered in quantum mechanics courses, so it is likely that your school may even have a Mössbauer apparatus in the Physics department. The Mössbauer effect is used to study many different types of isotopes with long-lived, low-lying excited nuclear energy state such as ^{99}Ru , ^{151}Eu , ^{155}Gd , ^{193}Ir , ^{195}Pt and ^{197}Au . However, among all the elements, the isotope with the strongest recoil-free resonant absorption ^{57}Fe , and for this reason the vast majority of Mössbauer studies are done using ^{57}Fe . For more information on application of this technique to the study of minerals, consult the classic reference by Bancroft (1973) or Hawthorne (1988). Another more thorough summary can be found in a recent review paper (Dyar et al., 2006).

- Bancroft, G.M. 1973. Mössbauer spectroscopy: an introduction for inorganic chemists and geochemists. Wiley and Sons, New York, 251 pp.
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- DeGrave E, Vandenberghe RE, Dauwe C. 2005. ILEEMS: Methodology and applications to iron oxides. *Hyperfine Interactions*, 161 (1-4): 147-160.
- Dyar, M.D. Agresti, D.G., Schaefer, M., Grant, C.A., and Sklute, E.C. 2006. Mössbauer spectroscopy of earth and planetary materials. *Annual Reviews of Earth and Planetary Science*, 34, 83-125.
- Hawthorne, F.C. 1988. Mössbauer spectroscopy. *Reviews in Mineralogy*, 18, 255-340.
- May L, editor. 1971. *An introduction to Mössbauer spectroscopy*. New York: Plenum. 203 pp.
- McCammon, C.A. 1994. A Mössbauer milliprobe: Practical considerations. *Hyperfine Interactions*, 92, 1235-9.

Related Links

For more information about Mössbauer Spectroscopy follow the links below.

- [The Mössbauer Effect Data Center](#) ([This site may be offline.](#)) provides information resources to Mössbauer researchers around the world, including databases, handbooks, searches, conference postings, and other useful information.
- [This site](#) gives educational information about Mössbauer spectroscopy, and background on how the technique is being used on Mars. [Its database](#) contains over 3,000 Mössbauer spectra of rock-forming minerals acquired at temperatures from 4-300K.

Other Resources on Mineral Spectroscopy

- [The Mineral Spectroscopy Server](#)--from George Rossman, CalTech
- [Spectroscopy](#)--NASA, GSFC
- [Spectroscopy of Rocks and Minerals](#) ([more info](#)) --from USGS, principles of spectroscopy
- [Spectroscopy Now](#)
- [Mars mineral spectroscopy database](#) ([more info](#)) --Mt Holyoke College

Teaching Activities and Resources

Teaching activities, labs, and resources pertaining to Mössbauer Spectroscopy.

- [Mars Exploration Rover and Beagle 2 Missions](#)