Mössbauer Spectroscopy of Earth and Planetary Materials

M. Darby Dyar,1,2 David G. Agresti,3 Martha W. Schaefer,4 Christopher A. Grant,5 and Elizabeth C. Sklute2

1Department of Earth and Environment and 2Department of Astronomy, Mount Holyoke College, South Hadley, Massachusetts 01075-1429; email: mdyar@mtholyoke.edu, ecsklute@mtholyoke.edu
3Department of Physics, University of Alabama at Birmingham, Birmingham, Alabama 35294-1170; email: agresti@uab.edu
4Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana 70803; email: schaefer@geol.lsu.edu
5Department of Chemistry, University of Oregon, Eugene, Oregon 97401

Key Words
resonant absorption, recoil-free fraction, iron valence state, iron site occupancy, quadrupole splitting distribution

Abstract
The field of Mössbauer spectroscopy (MS) has recently enjoyed renewed visibility in the diverse geoscience communities as a result of the inclusion of Mössbauer spectrometers on the Mars Exploration Rovers. Furthermore, new improvements in technology have made possible studies involving very small samples (1–5 mg or less) and samples with very low Fe contents (such as feldspars), in addition to samples measured in situ in thin sections. Because of these advances, use of Mössbauer spectroscopy in Earth science applications is expected to continue to grow, providing information on site occupancies; valence states; magnetic properties; and size distributions of (largely) Fe-bearing geological materials, including minerals, glasses, and rocks. Thus, it is timely to review here the underlying physics behind the technique, with a focus on the study of geological samples. With this background, recent advances in the field, including (a) changes in instrumentation that have allowed analysis of very small samples and of surface properties, (b) new models for fitting and interpreting spectra, and (c) new calculations of recoil-free fraction, are discussed. These results have made possible increasingly sophisticated studies of minerals, which are summarized here and organized by major mineral groups. They are also facilitating processing and interpretation of data from Mars.
INTRODUCTION

The technique of Mössbauer spectroscopy (MS) has long shared with wet chemistry the distinction of being a gold standard for determinations of Fe$^{3+}$ and Fe$^{2+}$ in solid materials, including a host of geological materials. The primary limitation of both techniques has traditionally been their need for significant masses of powdered samples, a restriction that has confined their usefulness to large samples and made difficult the study of rock-forming minerals within many important rock types for which obtaining large, pure mineral separates may be difficult.

For smaller samples, alternative techniques have been developed for Fe$^{3+}$/Fe$^{2+}$ measurements, but each has its own problems. Many workers have attempted to use electron microprobe analyses to calculate Fe$^{3+}$ and Fe$^{2+}$ on the basis of charge balance, but repeated studies have shown that this is limited to specific mineral groups, such as spinels (Wood & Virgo 1989), or impractical, especially for silicates (Canil & O’Neill 1996, Dyar et al. 1989, Sobolev et al. 1999). In optical spectroscopy, Fe$^{3+}$ peaks may be difficult to quantify because orientation must be controlled, the peaks lie at low energies near the UV, and electronic interactions among species can complicate interpretations. The inherent anisotropy of the majority of minerals also adds uncertainty to other promising techniques for measurement of Fe$^{3+}$ and Fe$^{2+}$ by other microbeam methods, such as X-ray photoelectron spectroscopy (XPS) (Nesbitt et al. 2004), electron-energy loss spectroscopy (EELS) (Garvie et al. 2004), and synchrotron X-ray absorption near-edge spectroscopy (XANES) (Dyar et al. 2002a). Milliprobe Mössbauer measurements have also found wide application (McCammon 1994, Sobolev et al. 1999). Despite these recent advances, the dominant technique for measuring Fe$^{3+}$ and Fe$^{2+}$ in geological materials remains conventional Mössbauer spectroscopy on powdered samples.

Papers describing the use of MS in mineralogy first appeared in the early 1960s (Pollak et al. 1962, de Coster et al. 1963), followed by a systematic investigation of common rock-forming minerals by Bancroft and Burns within 10 years of Mössbauer’s original discovery (e.g., Bancroft 1967, 1969; Bancroft & Burns 1967, 1969; Bancroft et al. 1967a,b,c, 1971; Bancroft & Brown 1975). Use of the technique continues to grow, with generally more than 100 studies of the Mössbauer effect in minerals published each year since the 1970s. Most recently, application of the technique has moved from the realm of pioneering mineralogical characterization to routine application to a steady stream of geological problems, moving from spectroscopy into geoscience. For the latter community, we have long recommended Bancroft’s (1973) seminal book, Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists, for geologically applied background information on the technique, but that publication is getting rather out of date.

Thus, the goal of this review is to create an accessible summary of the Mössbauer technique in its current implementation, to inform students and collaborators, to introduce new users to its capabilities, and to generally advance and advocate for this area of research. Accordingly, four major sections are included: a summary of the physics behind the Mössbauer effect, how it is applied to mineralogical studies, how...
current instrumentation and data processing are accomplished, and a brief overview of new directions for the technique.

**HOW THE MÖSSBAUER EFFECT WORKS**

**Fundamentals of Resonant Absorption**

Recoilless nuclear resonance was discovered by Mössbauer during his graduate studies at Heidelberg in 1957. It relies on the principle of resonant absorption of nuclear gamma rays in solids. Early discussions of the technique appear in Frauenfelder (1962), who summarizes important early developments and provides reprints of major early works, and Wegener (1965), who provides a thorough grounding in the theory of the spectroscopy.

Many geoscientists are already familiar with the concept of resonant absorption from the perspective of electronic events. When the energies of 3\(d\) orbitals in transition metals are split, it becomes possible for electrons to undergo a transition between orbitals when energy is added. This is one of the most common causes of colors in minerals. Only very specific energies (wavelengths) of light can lead to such resonant absorption phenomena.

An analogous process occurs with the addition or loss of energy to the energy levels in the nucleus. An isolated atom in an excited nuclear state \(E_e\) (such as a radioactive isotope) will decay and give off a gamma ray or transfer the transition energy to an atomic electron. If we assume for simplicity that the departing gamma photon carries away the entire energy \((E_\gamma; \text{Figure 1}, \text{top})\), and the gamma photon then impinges on another, identical atom, it can be absorbed by resonant capture. The absorber nucleus may then deexcite by emitting another gamma photon (Figure 1, bottom). As for atomic electrons, resonance absorption requires that the photon have exactly the correct quantized transition energy.

However, the excited state has a finite lifetime, \(\tau\). According to the Heisenberg uncertainty principle, the energy of the emitted gamma ray is then not precisely defined, but rather obeys a Breit-Wigner, or Lorentzian, distribution (Figure 1, top), centered on \(E_0\) with full width at half maximum, \(\Gamma_0\), given by \(\Gamma_0 = \hbar/\tau\), where \(\hbar\) is Planck’s constant divided by \(2\pi\).

The previous model assumes that the departing gamma photon carries away the entire energy of the nuclear transition, i.e., \(E_\gamma = E_0\). In fact, the photon has momentum, \(p_\gamma = E_\gamma/c\), where \(c\) is the speed of light. If we assume the emitting atom is isolated and initially at rest, then conservation of momentum dictates that it must recoil with momentum, \(p_{\text{nucleus}} = -p_\gamma\), and acquire a recoil energy, \(E_R\), given by

\[
E_R = \frac{(p_{\text{nucleus}})^2}{2M} = \frac{(-p_\gamma)^2}{2M} = \frac{E_\gamma^2}{2Mc^2},
\]

where \(M\) is the mass of the emitting nucleus. By conservation of energy, the transition energy is then shared between the nuclear recoil and the emitted photon, whose energy is thus reduced to \(E_\gamma = E_0 - E_R\). Similarly, a photon that can be absorbed
Figure 1
Idealized representation of the process of nuclear resonance fluorescence.
The source in an excited nuclear state decays and, in a first-excited- to
ground-state transition (top), gives off a gamma photon with an energy
that obeys a Breit-Wigner, or Lorentzian, distribution centered on
$E_0$. When the gamma photon impinges on another absorber atom
(bottom), it can be absorbed by resonant capture, subsequently
emitting a gamma photon of the same energy as the nucleus returns to its
ground state.

by an isolated atom at rest in a nuclear transition of energy $E_0$ must possess an
additional energy, $E_R$, to allow for the nuclear recoil. Thus, to be resonantly absorbed,
$E_\gamma = E_0 + E_R$.

Although the recoil energy ($10^{-4}$–$10^{-1}$ eV for free atoms) (Greenwood & Gibb
1971) is considerably smaller than the gamma energy ($10^1$–$10^5$ eV), it is still so large
relative to the gamma energy distribution represented by the linewidth shown in
Figure 1 ($10^{-9}$–$10^{-6}$ eV) that a nuclear resonant emission-absorption process cannot
occur between free atoms at rest.

On the other hand, if the emitting nucleus were moving toward the absorbing
nucleus with a relative velocity, $v$, the energy of the emitted gamma photon would be
Doppler shifted by an amount,

$$\Delta E_\gamma = E_\gamma (v/c).$$

In principle, the resonance process could occur if $v$ were sufficiently large ($\sim$4–
4000 m/s) that $\Delta E_\gamma = 2 E_R$, for then the emitted photon would have energy $E_\gamma = E_0 + E_R$, precisely what is required for absorption. However, this is highly impractical
because of the extreme narrowness of the photon distribution relative to $E_R$ and the
large velocities that would have to be produced with very high accuracy.

In reality, atoms are found in gases, liquids, or solids, and thus exhibit thermal mo-
tion with kinetic energy on the order of $k_B T$, where $k_B$ is Boltzmann’s constant and $T$
is the absolute temperature. At room temperature, $T \sim 300 \, \text{K}$ and $k_B \, T \sim 0.025 \, \text{eV}$, on the order of magnitude of $E_R$. By the Doppler effect, a comparable amount of energy is either added to, or subtracted from, an emitted gamma photon, depending on the direction of motion of the emitting nucleus, and a thermally broadened distribution of emitted photon energies is the result. A similar circumstance applies with respect to the energy required for resonant absorption. Thus, the nuclear recoil may be partially compensated by thermal motion and a certain amount of resonant absorption may occur.

The preceding argument suggests that as temperature is lowered, the thermally broadened distributions become narrower and absorption is reduced, eventually to zero at the lowest temperatures. This is what Mössbauer initially observed in his experiments, but as the temperature approached that of liquid nitrogen, contrary to expectations, the absorption increased dramatically (Mössbauer 1958). The explanation for this phenomenon, the Mössbauer effect, is not to be found in the foregoing discussion but rather in the quantized nature of the vibrational spectrum of a solid. Because a correct theoretical treatment (e.g., Mössbauer 1958, Visscher 1960) is beyond the scope of this work, we illustrate here the principal ideas by means of a highly simplified model.

A solid (with harmonic interatomic forces) may be regarded as consisting of a large number (three times the number of atoms) of vibrational modes, each one involving, in principle, all the atoms of the solid. In the Debye model, there is a distribution of vibrational frequencies. In the simple Einstein model, which we assume for now, each mode has a single characteristic vibrational frequency, $\omega$. The energy of each simple harmonic mode is then quantized such that

$$E_{SHM} = (n + \frac{1}{2}) \hbar \omega,$$

where $n = 0, 1, 2, \ldots$ is the vibrational quantum number, or the number of phonons associated with the energy state. In emission or absorption of a gamma photon by a nucleus, $n$ (the phonon number) may or may not change (increase or decrease). If it stays the same, the photon is absorbed in a zero-phonon process because no phonons are created ($n$ does not increase) or destroyed ($n$ does not decrease).

When a photon is emitted or absorbed by a nucleus, the solid takes up or releases vibrational energy ($n$ may change); the precise amount is predicted from a probability distribution. In a theoretical work remarkable for its simplicity and insight, Lipkin (1960) showed that the energy imparted to a crystal, averaged over a large number of emitted gammas, is exactly equal to the recoil energy, $E_R$.

We now apply the simplifying assumption of an Einstein model, that is, there is only one frequency, $\omega$. Let us assume that $E_R < \hbar \omega$ (Figure 2a) and that, during the emission of a gamma photon, $n$ either stays the same or increases by exactly 1, i.e., the solid undergoes a zero- or a one-phonon transition. (In a zero-phonon transition, the recoil momentum is picked up by the entire solid and, because of its large mass, $M$, according to Equation 1, the recoil energy is negligible.) Define the symbol $f$ to be the fraction of zero-phonon transitions, known also as the recoil-free fraction. Then the average energy given to the crystal is $(1-f) \hbar \omega$. Thus, according to Lipkin
Figure 2
Vibrational energy levels in a solid (schematic). (a) The recoil energy $E_R$ of an emitted gamma photon is less than that required 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. Thus, a gamma ray would be emitted without losing energy to the solid in a zero-phonon transition. This forms the basis for Mössbauer spectroscopy. (b) $E_R$ is significantly greater in energy than the lowest excitation energy of the solid ($E_{n+1} - E_n$). 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. Adapted from May (1971).

(1960), $E_R = (1 - f) \hbar \omega$, and in turn (in this simple model),

$$f = 1 - E_R / \hbar \omega.$$  

For $E_R > \hbar \omega$ this simple model fails, but then zero-phonon transitions also become much less likely (Figure 2b).

Clearly, larger values of $f$ are desirable. Thus, the Mössbauer effect (zero-phonon transition) is enhanced for smaller $E_R$, or, according to Equation 1, smaller gamma photon energies. We also see from Equation 4 that larger values of $\hbar \omega$ are desirable, which correspond to larger Debye temperatures.

More generally, and independently of the particular vibrational model of the solid, it can be shown (Frauenfelder 1962, equation 56) that

$$f = \exp \left[ -\langle x^2 \rangle E_R^2 / (\hbar c) \gamma^2 \right],$$

where $x$ is the component of nuclear displacement from its equilibrium position in the direction of the emitted (or absorbed) gamma photon, and $\langle x^2 \rangle$ is known as the mean-squared displacement (MSD) or the mean-square vibrational amplitude. From Equation 5, it is evident that there is also temperature dependence for $f$ because higher temperatures lead to larger $\langle x^2 \rangle$ or, equivalently, larger values of $n$ and a corresponding higher probability that $n$ will change, hence smaller values for $f$.

Finally, the Mössbauer effect cannot occur in gases or liquids (other than highly viscous ones) because for them translational motion is also possible, in which case
the quantum states are so closely spaced that $E_R$ is always very much greater than the spacing between energy levels, and $f = 0$.

**Mössbauer Spectroscopy of $^{57}$Fe**

What is it that makes $^{57}$Fe special? In principle, the Mössbauer effect applies to any and all nuclides, but in practice, certain ideal properties are desirable; that is, the conditions for recoil-free emission and absorption of gamma rays must be optimized. Most importantly, as seen in Equations 4 and 5, the energy of the nuclear transition must be small enough to yield a large recoil-free fraction, $f$. In other words, a large fraction of nuclear transitions must be zero-phonon transitions. The lifetime of the excited nuclear state, which determines the linewidth, should be neither too long (resulting in undue sensitivity to vibration) nor too short (resulting in loss of resolution). A parent of sufficient half-life must exist that can populate the excited nuclear states in a selected nuclide. Finally, the Mössbauer isotope must have sufficient natural abundance that meaningful experiments can be accomplished. The vast majority of Mössbauer studies use $^{57}$Fe, although the effect has been exploited in numerous other isotopes including $^{119}$Sn, $^{61}$Ni, $^{195}$Pt, and $^{197}$Au.

Fe is the most commonly occurring multivalent element in the terrestrial planets, which makes it particularly important for geological studies. Although only 2.2% of natural Fe atoms are the $^{57}$Fe isotope, its large $f$($\sim 0.65–1$) makes high-quality Mössbauer measurements possible. Its parent isotope is $^{57}$Co, which has a 270-day half-life and decays primarily to the 136.3-keV level of $^{57}$Fe (Figure 3) following capture of an atomic electron. Approximately 9% of the time, deexcitation is directly to the ground state with emission of a 136.3-keV gamma photon. Otherwise, decay is to the 14.4-keV state and then to the ground state with a half-life of $97.7 \times 10^{-9}$ s (lifetime, $\tau = t_{1/2}/\ln 2 = 141$ ns).

Of the 14.4 keV transitions, $\sim 11\%$ result in emission of a gamma ray, whereas the remaining 89% result in transfer of the transition energy to an atomic electron (electron conversion). A number of events can occur following electron conversion. There is emission of the conversion electrons (K, L, M) from the atom; they carry energy, $E_0 = 14.4$ keV minus their binding energy. That electron can then be absorbed by a second atom, leading to emission of a characteristic X-ray photon. Or, because the Fe atom must undergo some electronic rearrangement to accommodate the vacancy that results, emission of characteristic X-rays and possibly Auger electrons may occur (Figure 3). Electrons characteristically have limited escape depths in comparison to photons of comparable energy, but they are quite useful for studying mineral surfaces (see DeGrave et al. 2005 for a more in-depth discussion).

Various examples of the use of electrons emitted following nuclear resonant absorption include the following:

Figure 3
The nuclear decay scheme for $^{57}\text{Co} \rightarrow ^{57}\text{Fe}$ and various backscattering processes for $^{57}\text{Fe}$ that can follow resonant absorption of an incident gamma photon, modified from DeGrave et al. (2005).

- Depth-selective conversion electron Mössbauer spectroscopy (DCEMS) uses the 7.3 keV K-conversion or the 13.6 keV L-conversion electrons to probe at depths of a few nanometers (Liljequist & Ismail 1985, Liljequist et al. 1985, Pancholi et al. 1984).
- Integral low-energy electron Mössbauer spectroscopy (ILEEMS) detects low-energy electrons, also at a few nanometer depths, which has exciting potential for studies of mineral surfaces (Klingelhöfer & Kankeleit 1990, Klingelhöfer & Meisel 1990, DeGrave et al. 2005).
- Simultaneous gamma, X-ray, and electron Mössbauer spectroscopy (SGXEMS) measured gamma rays, x-rays, conversion electrons, and Auger electrons, all at the same time, using proportional gas flow detectors (Kamzin & Vcherashnii 2002). This technique allows the surface, subsurface, and interior of a sample to be analyzed.

Mössbauer Parameters
Mössbauer parameters are derived from a Mössbauer spectrum. So how is such a spectrum acquired? This may be seen from Figure 4, which shows three types of spectra: (brown) the emission spectrum (energy distribution of emitted gamma photons), Doppler modulated by moving the source, see Equation 2; (red) the absorption spectrum (probability of resonant absorption); and (blue) the transmission spectrum,
To form a Mössbauer spectrum, the source is moved to Doppler shift the center of the emission spectrum (brown) from smaller to larger energies, relative to the center of the absorption spectrum (red), whose center, the quantized transition energy, is fixed. The level of the transmission spectrum (blue) at each value of velocity, \( v \), is determined by how much the shifted emission spectrum overlaps the absorption spectrum, such that greater overlap results in reduced transmission owing to resonant absorption. The evolution of the transmission spectrum from large negative (source moving away from absorber) to large positive values of velocity may be followed from the top to the bottom rows of the figure. Figure courtesy of E. DeGrave.

**Figure 4**

![Mössbauer Spectrum Diagram](image)

What makes Mössbauer spectroscopy useful as an analytical tool is the fact that the nuclear energy levels may be modified (shifted and split apart) by the nuclear electronic environment. This is known as hyperfine interaction, and the parameters involved are products of fixed nuclear and variable electronic properties. Transitions between split levels may occur, as shown in Figure 5, resulting in generally more complex absorption spectra than the single-line pattern of Figure 4. 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, Figure 5), with each set corresponding to an acquired while detecting the 14.4-keV gamma rays that pass through the absorber. As the source velocity is varied, the emission spectrum is gradually changed from having no overlap with the absorption spectrum, to maximal overlap, and back again to no overlap. Where overlap is small, the count rate is large, and where overlap is large, the count rate is small owing to resonant absorption. As we follow the evolution of the spectrum from top to bottom in Figure 4, the transmission spectrum (blue) is gradually traced out as the velocity is varied from a large negative value (source moving away from the absorber), through zero, to a large positive value.

**Hyperfine interaction:** interaction between the nucleus and its surrounding electrons, leading to changes in the nuclear (and electronic) energy levels on the order of \( 10^{-7} \)–\( 10^{-8} \) eV. These changes provide information that enables characterization of the host material.
Isomer shift (IS): shift up or down of nuclear levels that results from overlap of nuclear and s-electron charge distributions

Figure 5
When unsplit source and absorber atoms are in different local environments, their nuclear energy levels are different. 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 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 the lower right ($m_I = -1/2$ to $+3/2$ and $m_I = +1/2$ to $-3/2$) do not occur owing 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.

Iron nucleus in a specific environment in the sample (a 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, a room-temperature spectrum of a given mineral may consist of a superposition of doublets and sextets.

Generally, the local environments around Fe atoms in source and absorber are not the same, and the absorption spectrum will not be centered on zero relative energy. This will result in an offset from zero velocity in the transmission spectrum, which is variously called isomer shift, chemical shift, or center shift, and is commonly
denoted by IS or δ (Figure 5, blue). The shift results from a Coulombic interaction between the nuclear and electronic charge distributions, and is strictly a function of the v-electronic charge density at the nucleus, although this density is also affected by shielding from p, d, and f electrons and by participation of electrons in bonding. IS values are generally reported relative to some standard absorber, usually α-Fe, although sodium nitroprusside \([\text{Na}_2\text{Fe(CN)}_6\text{NO}_2\text{H}_2\text{O}]\), which is shifted relative to α-Fe by \(-0.257 \text{ mm/s}\), is sometimes used in older papers.

In minerals, the local point symmetry of the electronic environment at the nucleus is rarely cubic. Then, the nuclear quadrupole moment (the effective shape of the ellipsoid of nuclear charge distribution) interacts with the gradient of the electric field that arises from other charges in the crystal to split the nuclear energy levels (Figure 5, red). This splitting is called quadrupole splitting, or electric quadrupole splitting, and is variously denoted by QS, Δ, or ΔEQ. The phenomenon is very much analogous to the splitting of 3d orbitals that occurs in transition metals as a result of crystal field splitting. As shown in Figure 5 (red), QS has the effect of causing the \( I = \frac{3}{2} \) level to split into two sublevels (I is the nuclear spin quantum number of the level). In a doublet, QS is defined as the separation between the two component peaks, i.e., the difference of the two transition energies.

Because the \(^{57}\text{Fe}\) nucleus possesses a magnetic moment, its energy levels can be perturbed if a magnetic field is present, as for magnetically ordered materials (e.g., ferrimagnetic materials such as magnetite) or if an external magnetic field is applied, resulting in magnetic hyperfine (Zeeman) interaction. The effect is to completely remove the degeneracy of the nuclear energy levels. They split into six different levels (Figure 5, green), with the \( I = \frac{1}{2} \) level splitting into two and the \( I = \frac{3}{2} \) level splitting into four sublevels, which are labeled with \( m_I \), the z projection of the nuclear spin. When transition selection rules are included (|Δ\( m_I | \leq 1\)), as is typically correct for minerals, the resultant Mössbauer spectrum is a sextet. Although the linewids of the six lines are in principle equal, their intensities are very different. In a randomly oriented sample, for an ideal thin absorber, the area ratios of the six lines are in proportion to the Clebsch-Gordan coupling coefficients, namely, 3:2:1:1:2:3 (Figure 5, green). As with quadrupole splitting, the IS of the sextet is the center of gravity of the six peaks.

For combined quadrupole and magnetic hyperfine splitting, the situation is more complex owing to mixing of states (cf. Wegener 1965). If the electric quadrupole interaction is small (leading to small shifts in line positions, \( \delta \), of the magnetic sextet pattern, as is the case for hematite), the quadrupole shift parameter is defined as QS = \( (l_6 - l_5) - (l_2 - l_1) \), with peaks numbered from left to right. Although the same symbol is used as for the quadrupole splitting, the two are identical only in special cases because the quadrupole shift depends on the relative directions of the magnetic field and the principal axis of symmetry of the electric field gradient tensor.

To determine the magnitude of the magnetic hyperfine field, \( B_{hf} \), in tesla (T), use is made of the relations \( \Delta E_g = |g| \mu_N B_{hf} \) and \( \Delta E_{ps} = |g^*| \mu_N B_{hf} \), where \( g \) is the nuclear g-factor and \( \mu_N \) is the nuclear magneton. The entire sextet pattern is fit to determine the ground-state splitting, \( \Delta E_g \), in millimeter per second, while constraining \( \Delta E_{ps}/\Delta E_g = g^*/g = -0.5714(1) \). Then \( B_{hf} \) is computed according to

**Electric quadrupole interaction:** orientation of the nuclear quadrupole moment (spin \( I \geq 1 \)) in a distribution of electronic charge lacking spherical or cubic symmetry (electric field gradient \( \neq 0 \)). This leads to a quadrupole splitting of (or quadrupole shift of already split) nuclear levels, designated QS

**Magnetic hyperfine interaction:** orientation of the nuclear magnetic moment (spin \( I \geq 1/2 \)) in an effective magnetic field, \( B_{hf} \), that arises from magnetic order or is externally applied. This leads to complete removal of degeneracy (i.e., full splitting) of the nuclear levels.
\[ B_{hf} = \Delta E_g \cdot 8.416 \, \text{T(mm/s)}^{-1} \], where \( g = 0.181208(9) \) and \( \mu_N = 3.1525 \times 10^{-8} \) eV/T = 0.65572 (mm/s)/T. [From Equation 2, 4.80766(3) \times 10^{-8} \) eV is equivalent to 1 mm/s for \(^{57}\)Fe.] Values are from MEDI (Stevens 1974), with errors in parentheses.

Many common rock-forming minerals exhibit magnetic ordering at low temperatures. This has the effect on the spectra of splitting doublets into sextets or even octets (see below) over a range of temperature, such that in the temperature regime over which this transition occurs, doublets and hyperfine patterns may appear for the same site. Spectra taken over such a transition temperature range are typically difficult to impossible to fit, however comparison of spectra above and below the transition temperature is very valuable in determining the crystal environment of the iron in the sample.

Some minerals, for example, fayalite, Fe\(_2\)SiO\(_4\) (Kundig et al. 1967), exhibit not a six-line pattern at low temperature, but an eight-line pattern. This is due to the relaxation of the transition selection rules to allow spin-forbidden transitions (\(|\Delta m_I| = 2\)), which occurs when the orientation of the nuclear magnetic moment is not parallel to the magnetic field of the nucleus (Schaefer 1983a,b).

**Significance of Mössbauer Parameters**

The combination of IS 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 (Figures 6 and 7). 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 Figures 6 and 7, Fe atoms in minerals are predictably found in coordination polyhedra of appropriate size based on radius ratios. As shown in Table 1, Fe\(^{3+}\) occurs primarily in 4- or 6-coordination with oxygen, whereas Fe\(^{2+}\) may be rarely 4- or 5-coordinated, commonly 6-coordinated, and occasionally 8-coordinated with oxygen. Fe in 4-coordination with sulfur has subtly different parameters owing 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).

Rock-forming minerals on Earth most commonly contain Fe\(^{2+}\) in octahedral coordination (c.f. Pauling’s Rules), and thus have very similar Mössbauer parameters. For example, pyroxene, amphibole, and mica spectra are all nearly indistinguishable (Table 1). Furthermore, most minerals exhibit a range of Mössbauer parameters as a function of cation substitution, so the values given in Table 1 should be viewed only as starting points! Finally, the parameters vary as a function of temperature, and the magnitude of that variation is distinctive to each mineral composition (see further discussion of \( \phi \) below). For these reasons, Mössbauer spectroscopy is not ideally suited to mineral identification and is typically not used for this purpose (though it has been pressed into such service in extraterrestrial applications).
Figure 6

(Top) Room temperature isomer shift versus quadrupole splitting data for common rock-forming minerals, taken from Table 1 and Burns & Solberg (1988). Oxides are shown in purple; sulfides, sulfates, and phosphates in orange; and silicates in green. (Bottom) Fairly distinctive ranges occur for each valence state and site occupancy of Fe, as labeled; note that fivefold coordination would lie between 4- and 6-coordination. Between the ranges for Fe$^{3+}$ and Fe$^{2+}$ is a poorly defined region where 0.5 > IS > 0.9 mm/s (blue rectangle); doublets with those parameters are generally taken to represent delocalization of electrons between adjacent Fe$^{3+}$ and Fe$^{2+}$, resulting in an averaged value of IS that can be assigned to Fe$^{2.5+}$. Because quadrupole splitting reflects site distortion, relative values of QS can be used to compare polyhedral distortion in spectra of minerals where two sites with the same coordination number are found; these tendencies toward regular versus distorted polyhedra are shown here. These ranges are used to infer valence state and coordination number of Fe atoms in minerals where they are unknown. They are best used to interpret spectral parameters from silicates; oxides, sulfides, etc., tend to have broader ranges of parameters.
Figure 7
Mössbauer spectra of mineral species representing the regions shown in Figure 6 (mineral group names are given in parentheses; staurolite does not belong to any group). Tetrahedral Fe$^{3+}$ dominates the spectrum of an unusual nonmarine glauconite from Hurricane Mountain, New Hampshire (sample courtesy of Carl Francis). The jarosite structure contains Fe$^{3+}$ (OH)$_2$O$^2$ octahedral rings; this sample is a synthetic composition, #14B from Brophy & Sheridan (1965). Staurolite is one of the few common mineral species to contain tetrahedral Fe$^{2+}$; the sample shown here is 356-1 from Dyar et al. (1991). Olivine is a typical silicate containing octahedral Fe$^{2+}$; this forsterite is from San Carlos (unpublished data). Almandine from Fort Wrangell, Alaska, here represents the Mössbauer spectrum of Fe$^{2+}$ in pseudocubic, eightfold coordination in the garnet structure (Dyar 1984). Spectra are normalized to 4% absorption and stacked with a 3% offset for clarity. All data collected in Dyar's laboratory.
Table 1  Typical 295 K Mössbauer parameters of rock-forming minerals

<table>
<thead>
<tr>
<th>Dana class</th>
<th>Species or group name</th>
<th>IS</th>
<th>QS</th>
<th>Site or Bhf</th>
<th>References(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native element</td>
<td>Iron</td>
<td>0.00</td>
<td>0.00</td>
<td>33.1</td>
<td>Various workers</td>
</tr>
<tr>
<td>Sulfides</td>
<td>Chalcocite</td>
<td>0.33</td>
<td>0.56</td>
<td>Music et al. (1981)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bornite</td>
<td>0.36</td>
<td>0.21</td>
<td>Gallup &amp; Reiff (1991)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sphalerite</td>
<td>0.60</td>
<td>0.63</td>
<td>Various workers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Troilite</td>
<td>0.77</td>
<td>−0.08</td>
<td>31.3</td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td>Stannite</td>
<td>0.52</td>
<td>2.91</td>
<td>Baldini et al. (1989)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pyrite</td>
<td>0.29</td>
<td>0.60</td>
<td>Various workers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Marcasite</td>
<td>0.28</td>
<td>0.49</td>
<td>Various workers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Arsenopyrite</td>
<td>0.30</td>
<td>1.15</td>
<td>Various workers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tochalinite</td>
<td>1.16</td>
<td>2.77</td>
<td>This work; preliminary results</td>
<td></td>
</tr>
<tr>
<td>Sulfosalts</td>
<td>Franckite</td>
<td>0.23</td>
<td>0.55</td>
<td>Huang (1987)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tetrahedrite</td>
<td>0.34</td>
<td>0.43</td>
<td>Charnock et al. (1989)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tennantite</td>
<td>0.51</td>
<td>2.22</td>
<td>Makovicky et al. (2003)</td>
<td></td>
</tr>
<tr>
<td>Simple oxide</td>
<td>Wüstite</td>
<td>0.95</td>
<td>0.44</td>
<td>Murad &amp; Johnston (1987)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hematite</td>
<td>0.37</td>
<td>−0.20</td>
<td>51.8</td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td>Ferricyanide</td>
<td>0.35</td>
<td>0.83</td>
<td>Murad &amp; Johnston (1987)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ilmenite</td>
<td>1.04</td>
<td>0.70</td>
<td>Virgo et al. (1988)</td>
<td></td>
</tr>
<tr>
<td>Hydroxide</td>
<td>Goethite</td>
<td>0.37</td>
<td>−0.26</td>
<td>38.2</td>
<td>Murad &amp; Johnston (1987)</td>
</tr>
<tr>
<td></td>
<td>Lepidocrocite</td>
<td>0.37</td>
<td>0.53</td>
<td>Murad &amp; Johnston (1987)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Akaganéite</td>
<td>0.38</td>
<td>0.53</td>
<td>Murad &amp; Johnston (1987)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ilmenite</td>
<td>1.04</td>
<td>0.70</td>
<td>Virgo et al. (1988)</td>
<td></td>
</tr>
<tr>
<td>Oxide</td>
<td>Hercynite</td>
<td>0.82</td>
<td>1.62</td>
<td>Murad &amp; Johnston (1987)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Magnetite</td>
<td>0.26</td>
<td>−0.02</td>
<td>49.0</td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td>Spinel</td>
<td>1.11</td>
<td>1.75</td>
<td>Various workers</td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
**Table 1 (Continued)**

<table>
<thead>
<tr>
<th>Dana class</th>
<th>Species or group name</th>
<th>IS</th>
<th>QS</th>
<th>Site or Bhf</th>
<th>References(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chromite</td>
<td>0.32</td>
<td>0.44</td>
<td></td>
<td>Kuno et al. (2000)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.22</td>
<td>0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.96</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.90</td>
<td>1.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ulvöspinel</td>
<td>1.07</td>
<td>1.85</td>
<td></td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td>Multiple oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Columbite</td>
<td>1.15</td>
<td>1.55</td>
<td></td>
<td>Garg et al. (1991)</td>
</tr>
<tr>
<td></td>
<td>Siderite</td>
<td>1.22</td>
<td>1.80</td>
<td></td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td>Ankerite</td>
<td>1.23</td>
<td>1.50</td>
<td></td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td>Anhydrous carbonates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrous carbonates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Szomolnokite</td>
<td>1.28</td>
<td>2.75</td>
<td></td>
<td>This work; preliminary results</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.65</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Römerite</td>
<td>1.29</td>
<td>3.30</td>
<td></td>
<td>This work; preliminary results</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.27</td>
<td>2.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.39</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.13</td>
<td>0.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Melanerite</td>
<td>1.25</td>
<td>2.86</td>
<td></td>
<td>This work; preliminary results</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.27</td>
<td>3.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.46</td>
<td>0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.18</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Halotrichite</td>
<td>1.28</td>
<td>2.73</td>
<td></td>
<td>This work; preliminary results</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.30</td>
<td>3.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.32</td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.45</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.14</td>
<td>0.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Coquimbite</td>
<td>0.11</td>
<td>0.63</td>
<td></td>
<td>This work; preliminary results</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.46</td>
<td>0.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.27</td>
<td>0.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Voltaitre</td>
<td>1.22</td>
<td>1.58</td>
<td></td>
<td>This work; preliminary results</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.34</td>
<td>1.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.46</td>
<td>0.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.17</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anhydrous sulfate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jarosite</td>
<td>0.37</td>
<td>1.20</td>
<td></td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>0.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrated phosphate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phosphoferrite</td>
<td>1.19</td>
<td>2.45</td>
<td></td>
<td>Mattieich &amp; Danon (1974)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.19</td>
<td>1.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vivianite</td>
<td>1.21</td>
<td>2.98</td>
<td></td>
<td>Anthauer &amp; Rossman (1984)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.18</td>
<td>2.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.38</td>
<td>1.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>0.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anhydrous phosphate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lazurite</td>
<td>1.12</td>
<td>3.32</td>
<td></td>
<td>Anthauer &amp; Rossman (1984)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Dana class</th>
<th>Species or group name</th>
<th>IS</th>
<th>QS</th>
<th>Site or B$_{hf}$</th>
<th>References(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrated phosphate</td>
<td>Strunzite</td>
<td>0.38</td>
<td>1.37</td>
<td></td>
<td>Vogel &amp; Evans (1980)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.41</td>
<td>0.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.41</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anhydrous tungstate</td>
<td>Ferberite</td>
<td>1.11</td>
<td>1.49</td>
<td></td>
<td>Caruba et al. (1982)</td>
</tr>
<tr>
<td>Orthosilicates</td>
<td>Willemite</td>
<td>1.02</td>
<td>2.92</td>
<td></td>
<td>Holtstam (2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.09</td>
<td>2.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fayalite</td>
<td>1.14</td>
<td>3.10</td>
<td>M</td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td>Forsterite</td>
<td>1.14</td>
<td>2.93</td>
<td>M</td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td>Zircon</td>
<td>0.27</td>
<td>1.03</td>
<td></td>
<td>Carreto et al. (2001)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21</td>
<td>51.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Almandine</td>
<td>1.29</td>
<td>3.53</td>
<td>8</td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td>Andradite</td>
<td>0.40</td>
<td>0.55</td>
<td>M</td>
<td>Various workers</td>
</tr>
<tr>
<td></td>
<td>Staurolite</td>
<td>0.98</td>
<td>2.44</td>
<td>Fe1</td>
<td>Dyar et al. (1991)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.98</td>
<td>2.08</td>
<td>Fe3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.97</td>
<td>1.55</td>
<td>Fe2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.89</td>
<td>0.93</td>
<td>Fe</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.05</td>
<td>0.83</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11</td>
<td>0.79</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Disilicates</td>
<td>Chloritoid</td>
<td>1.12</td>
<td>2.42</td>
<td>M</td>
<td>Koch-Muller et al. (2000)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.29</td>
<td>0.96</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pumpellyte</td>
<td>0.42</td>
<td>1.70</td>
<td></td>
<td>Artioli et al. (2003)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.34</td>
<td>1.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.20</td>
<td>2.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.09</td>
<td>3.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Epidote</td>
<td>1.07</td>
<td>1.62</td>
<td>M</td>
<td>Kartashov et al. (2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.36</td>
<td>1.78</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.33</td>
<td>0.85</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ferroaxinite</td>
<td>1.30</td>
<td>2.12</td>
<td></td>
<td>Astakhov et al. (1975)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.57</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ring silicates</td>
<td>Schorl (tourmaline)</td>
<td>0.17</td>
<td>0.51</td>
<td>T</td>
<td>Dyar et al. (1998)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.43</td>
<td>0.82</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.77</td>
<td>1.21</td>
<td>ED</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.09</td>
<td>2.47</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.09</td>
<td>2.19</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.07</td>
<td>1.60</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Beryl</td>
<td>1.16</td>
<td>2.70</td>
<td></td>
<td>Sample courtesy of L. Groat; preliminary results</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.59</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cordierite</td>
<td>1.19</td>
<td>2.30</td>
<td></td>
<td>Khomenko et al. (2001)</td>
</tr>
</tbody>
</table>

(Continued)
Table 1 (Continued)

<table>
<thead>
<tr>
<th>Dana class</th>
<th>Species or group name</th>
<th>IS</th>
<th>QS</th>
<th>Site or B&lt;sub&gt;20f&lt;/sub&gt;</th>
<th>References(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyroxenes</td>
<td>Ferrosilite</td>
<td>1.18</td>
<td>2.49</td>
<td>M1</td>
<td>Dowty &amp; Lindsley (1973)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.13</td>
<td>1.91</td>
<td>M2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hedenbergite</td>
<td>1.18</td>
<td>2.21</td>
<td>M1</td>
<td>Eeckhout &amp; DeGrave (2003)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.34</td>
<td>0.68</td>
<td>M1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diopside</td>
<td>1.16</td>
<td>1.87</td>
<td>M1</td>
<td>DeGrave &amp; Eeckhout (2003)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.15</td>
<td>2.14</td>
<td>M2</td>
<td></td>
</tr>
<tr>
<td>Pyroxenoid</td>
<td>Babingtonite</td>
<td>0.30</td>
<td>0.77</td>
<td>M</td>
<td>Burns &amp; Dyar (1991)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>0.84</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.20</td>
<td>2.41</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td>Amphiboles</td>
<td>Tremolite-actinolite</td>
<td>1.11</td>
<td>2.85</td>
<td>M1</td>
<td>Burns &amp; Greaves (1971)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.12</td>
<td>1.80</td>
<td>M2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.11</td>
<td>2.40</td>
<td>M3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kaersutite</td>
<td>1.11</td>
<td>2.05</td>
<td>M</td>
<td>Dyar et al. (1993)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.06</td>
<td>2.41</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.39</td>
<td>0.87</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Winchite</td>
<td>1.13</td>
<td>1.90</td>
<td>M2</td>
<td>Gunter et al. (2003)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.13</td>
<td>2.86</td>
<td>M1+M3</td>
<td></td>
</tr>
<tr>
<td>Chain silicate</td>
<td>Surinamite</td>
<td>0.35</td>
<td>0.53</td>
<td>M</td>
<td>Barbier et al. (2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.20</td>
<td>2.42</td>
<td>M1+M5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.12</td>
<td>2.02</td>
<td>M4+M7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.03</td>
<td>1.30</td>
<td>M8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.36</td>
<td>1.09</td>
<td>M2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.31</td>
<td>0.92</td>
<td>M3+M6 + M9</td>
<td></td>
</tr>
<tr>
<td>Sheet silicate</td>
<td>Clintonite</td>
<td>0.47</td>
<td>0.51</td>
<td>M</td>
<td>Wang &amp; Zhengmin (1992)</td>
</tr>
<tr>
<td></td>
<td>Chlorite</td>
<td>0.25</td>
<td>0.50</td>
<td>T</td>
<td>Smyth et al. (1997)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.09</td>
<td>2.59</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.11</td>
<td>2.33</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.14</td>
<td>2.66</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.12</td>
<td>0.39</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>0.40</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>0.65</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Illite</td>
<td>1.12</td>
<td>2.61</td>
<td>M</td>
<td>Murad &amp; Wagn (1994)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.36</td>
<td>0.61</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phlogopite</td>
<td>1.13</td>
<td>2.57</td>
<td>M</td>
<td>Various authors</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.12</td>
<td>2.15</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>0.87</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.20</td>
<td>0.75</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Talc</td>
<td>1.13</td>
<td>2.57</td>
<td>M</td>
<td>Coey et al. (1991)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.12</td>
<td>2.15</td>
<td>M</td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
Table 1 (Continued)

<table>
<thead>
<tr>
<th>Dana class</th>
<th>Species or group name</th>
<th>IS</th>
<th>QS</th>
<th>Site or Bhf</th>
<th>References(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kaolinite</td>
<td>0.41</td>
<td>0.46</td>
<td>M</td>
<td>Murad &amp; Wagner (1991)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.11</td>
<td>2.53</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Glaucnite</td>
<td>1.11</td>
<td>2.71</td>
<td>M</td>
<td>Ali et al. (2001)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.33</td>
<td>0.45</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.34</td>
<td>0.99</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lizardite</td>
<td>1.14</td>
<td>2.70</td>
<td>M</td>
<td>O’Hanley &amp; Dyar (1993)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>0.70</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.24</td>
<td>0.39</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chrysotile</td>
<td>1.13</td>
<td>2.75</td>
<td>M</td>
<td>O’Hanley &amp; Dyar (1998)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.31</td>
<td>0.86</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.18</td>
<td>0.33</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Framework silicates</td>
<td>Feldspar</td>
<td>1.14</td>
<td>2.12</td>
<td>M</td>
<td>Dyar et al. (2002b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.92</td>
<td>2.09</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.09</td>
<td>1.45</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.19</td>
<td>1.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.55</td>
<td>1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.24</td>
<td>1.19</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*All values of IS are referenced to the midpoint of an α-Fe spectrum. IS and QS are given in mm/s and Bhf in tesla. For site occupancies, T = tetrahedral site, M = octahedral site, and 8 = 8-coordination; in some cases, mineral-specific site names are given. If no assignment is given in the citation, none is given here. Shaded cells represent data for which information was not given.

IS is extremely sensitive to the oxidation state of the sample. IS values predictably decrease with increasing s-electron density around the nucleus, so they depend not only on oxidation state but also on the type and bond lengths of ligands coordinated to the Fe atoms. In minerals and silicate glasses, Mössbauer parameters are confined to relatively small ranges. Parameters for Fe$^{3+}$ cover a relatively small range in IS. In silicates and oxides, high metal-oxygen distances in coordination polyhedra result in higher values of isomer shift. The upper limit for Fe$^{3+}$ in tetrahedral coordination is approximately 0.25 mm/s, whereas the lower limit for octahedral Fe$^{3+}$ is approximately 0.29 mm/s (Burns & Solberg 1988). For Fe$^{2+}$, values of IS > 1.20 mm/s are generally attributed to eightfold or dodecahedral coordination, values of 1.20 > IS > 1.05 mm/s are generally octahedral, and values of 1.05 > IS > 0.90 mm/s are assigned to tetrahedral occupancy.

Quadrupole splitting is sensitive to oxidation state and site geometry. As an example, consider Fe$^{3+}$ in perfectly octahedral (sixfold) coordination. The electronic configuration of Fe$^{3+}$, $3d^5$, is in general high spin for minerals, i.e., $t_{2g}^3 e_{g}^2$. The sixth electron populates the three degenerate (all the same energy) $t_{2g}$ levels equally, so spherical symmetry is maintained and, neglecting lattice terms, there is no quadrupole splitting. A distortion of the octahedral environment, as occurs through Jahn-Teller
distortion, lifts the degeneracy of the $t_{2g}$ levels, leading to unequal occupancy of the $d$ orbitals and a large contribution to QS from the electronic field. In high-spin Fe$^{3+}$, which has electronic configuration $t_{2g}^2e_g^3$, the $d$ orbitals remain equally populated even when the octahedral environment is distorted, and the electronic field remains spherical. Of course, in both cases, asymmetry in the lattice field causes $[6]$Fe$^{2+}$ and $[6]$Fe$^{3+}$ to split the $I = 3/2$ level, but in general, QS for Fe$^{3+} \gg$ QS for Fe$^{2+}$. Furthermore (as a general rule), the larger the QS, the more distorted the coordination polyhedron surrounding the Fe atom.

For phases that show hyperfine splitting, the magnitude of the magnetic field can be useful in distinguishing among phases with similar IS and QS. This is useful in identification of such phases as iron oxides at room temperature and in low-temperature studies, comparing the hyperfine split low-temperature spectra to their simple quadrupole-split room-temperature counterparts.

Mössbauer parameters of minerals (and everything else!) can be found by searching the comprehensive online, subscription database maintained by the Mössbauer Effect Data Center (MEDC, at http://www.unca.edu/medc/). This resource, which includes all published Mössbauer papers back to and including Professor Rudolf L. Mössbauer’s original paper in 1958, contains over 80,000 records, is the result of a 30-year effort, and is updated monthly. Its strength, which lies in its incredible breadth of coverage, unfortunately somewhat limits its usefulness: Parameters listed there come from publications of all types and are simply reported from the literature without judgment of their reasonableness. Although the MEDC provides an excellent starting point for understanding Mössbauer parameters of any given material, it is always necessary to consult the original papers to evaluate the conditions and constraints with which data were generated.

The MEDC compiles parameters only. Our research group maintains an online library of Mössbauer spectra (and ASCII data) of many rock-forming minerals at www.mtholyoke.edu/courses/mdyar/database. Although our site is largely limited to data collected in our own laboratory, it presents typical spectra from many mineral groups, and is intended as a teaching resource for the community.

**INSTRUMENTATION**

The basic elements of a Mössbauer spectrometer are a source, a sample, a 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 a velocity of 1 mm/s toward the sample, by Equation 2, increases the energy of the emitted photons by $(14.413 \text{ keV}) \cdot (v/c) = 4.808 \times 10^{-8} \text{ eV}$, or approximately ten natural linewidths. Thus, “mm/s” 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 (cf. Handke et al. 2005). The location of the detector relative to the source and the sample defines the geometry of the experiment (Figure 8); most commonly, either transmission or backscatter modes are used.
Transmission Mode Experiments

The instrumentation for Mössbauer experiments is well described by Bancroft (1973) and updated by Murad & Cashion (2004), so only a brief update is needed here. The vast majority of Mössbauer experiments in the geosciences are conducted in transmission mode, where the gamma path leads directly from source to detector and just one event is of importance (resonant gamma absorption), the velocity is well defined, and, for a thin absorber (sample), the resulting spectrum is a simple superposition of spectra of the individual mineral components.

Recent major advances in spectrometer design have made it possible to study samples with either low total Fe contents or low sample mass; such a design is now
commercially available from WEB Research Co. of Minneapolis, MN. For the low sample masses, this involves use of a strong $^{57}$Co source (50–100 mg) as well as constraining the combination of source size, sample shielding, and alignment while minimizing the amplitude of the emitter (source) motion to make it possible to use samples with 0.5 cm mount diameter. This represents a sample area (which is filled with a mixture of sample plus a dispersing medium that acts as a filler, usually sucrose) that is only 5% of the sample area used in older instruments. This improvement in technology means the difference between handpicking 5–10 mg of pure mineral (a job that takes less than an hour even in extremely fine-grained samples) versus 200–300 mg (a week's job for the best pickers!).

The new instruments make it possible to position the source within only a few millimeters of the sample, even at 4.2K, while retaining linewidths of 0.22 mm/s for the central lines of an Fe foil. In our laboratory, this change in geometry initially doubled our count rates with a standard Kr gas counter and a single SCA counting system; the subsequent substitution of a scintillation detector improved count rates by an additional 60%. With the current apparatus, >1,000,000 baseline counts per hour can be acquired on a sample with ideal thickness when a 100 mCi source is used. Thus, a spectrum that once took 1–2 days to acquire can now be generated in one hour! Even with very short runs, data of outstanding quality can be acquired.

Data quality can be further enhanced by correcting for (nongamma) Compton scattering, which contributes to the background within the 14.4-keV single-channel analyzer window in every measurement. The “% Transmission” scale on Mössbauer plots can then be corrected to refer only to transmitted gamma photons. The fraction of the baseline owing to the Compton scattering of 136 keV and 122 keV gammas off counter gas electrons can be determined by measuring the count rate with and without a 14.4-keV stop filter in the gamma beam (we use $\sim$200 μm of Al foil). If $b$ is the Compton fraction and $A$ is the uncorrected absorption, then the Compton-corrected absorption is $A/(1 - b)$. This correction provides an absorption scale that is fairly independent of the type of gamma detector used, but it must be calculated for each individual sample. The resultant improvement is worth it.

**Mössbauer Milliprobe**

A highly successful adaptation of the powdered sample Mössbauer apparatus for transmission experiments has been the milliprobe developed by Catherine McCammon at Bayreuth (McCammon et al. 1991, 2000; McCammon 1994; Sobolev et al. 1999). This modification, which uses a lead plate to restrict gamma rays to a small diameter ($\sim$100 μm), can be used to study single grains in thin sections or single crystals. Its application is limited by the need to know the orientation of the electric field gradient (EFG) tensor in various mineral groups to overcome the texture effects imposed by study of anisotropic crystals; such work is indeed ongoing (e.g., Tennant et al. 2000). Many studies using the milliprobe technique have been made, most recently including Partzsch et al. (2004), McCammon et al. (2004a,b), and Bromiley et al. (2004).
**Backscatter Geometries**

Backscatter Mössbauer spectra (illustrated schematically in Figure 8b) are acquired while detecting radiation emitted by the sample/absorber as function of source velocity, either the 14.4-keV gamma or 6.4-keV X-ray photons. They contrast with transmission measurements, which simply report whether resonant absorption occurs, in that they incorporate multiple internal events, both nuclear and extranuclear (atomic). Source gammas strike the sample at various angles and initiate a complex series of events involving gamma photons, X-rays, and electrons, leading to a complex radiation path, which may be multiply branched. The detected radiation exits the sample at various angles before striking the detection surface and contributing to the backscatter spectrum, so that the interrogated portion of the rock or soil is not simply related to photoelectric attenuation coefficients for 14.4 keV and 6.4 keV.

Although the principles of backscatter theory are well established (e.g., Balko & Hoy 1974, Bara & Bogacz 1977, Bara 1980); and particular geometries have been modeled (e.g., Jaggi 1982, Fultz & Morris 1986, Mei 1987, Lefman 1991), until recently literature on its application has been sparse owing to its infrequent utilization in the laboratory. The application of the theory must be developed anew for each particular situation because it is strongly dependent on the geometry of both sample and backscatter instrument, in particular in the case where source, sample, and detector are all extended objects. To properly apply backscatter theory, the theory must incorporate all the various events that occur, and an optimal method for summing contributions to the observed backscatter spectrum must be developed, based on an integration over angles or a simulation of “paths” followed by individual incident gamma photons leading to the detected 14.4- or 6.4-keV photons, such as via so-called Monte Carlo methods.

The dramatically different geometry of the backscatter instrument makes proper interpretation significantly more complex than the usual transmission-mode experiments. Geometry-related considerations that must be taken into account for analysis of backscatter data include the following:

- Spread of $^{57}$Co nuclei in the Mössbauer source and appearance of resonantly absorbing $^{57}$Fe nuclei as the source ages (emission profile)
- Angular spread of emitted gamma photons (velocity profile)
- Distance of source from interrogated surface
- Area of interrogated surface exposed to source radiation
- Distribution of detector surfaces (silicon PIN detectors are used on the Mars rover instruments, discussed below)
- Differences in 14.4- and 6.4-keV spectra, i.e., those acquired while detecting gamma or Fe Kα X-ray photons

Despite the complexity in modeling backscatter measurements, they are the only practical application of this technique for planetary exploration. The remarkable Mössbauer instruments on the Mars Exploration Rovers (MERs), the MIMOS II spectrometers, are described in Klingelhöfer et al. (2003). Many examples of spectra obtained with MIMOS II and similar miniature backscatter instruments are available
in the literature (e.g., Klingelhöfer 1998; Shelfer & Morris 1999; Klingelhöfer et al. 2003, 2004; Wdowiak et al. 2003; Morris et al. 2004).

Analyses published by the MER team (Klingelhöfer et al. 2004, Morris et al. 2004) have provided dramatic new insights into the nature of Mars surface material, for example, suggesting the presence of minerals produced in the presence of water. However, to accommodate relatively poor counting statistics (compared to laboratory expectations), compromises in the data fitting were adopted by the MER team. These include summing of spectra acquired under different conditions, e.g., at variable temperatures, with consequent loss of information; modeling spectra as sums of Lorentzians, with limited consideration of geometric, i.e., saturation, effects that lead to line distortions; and ignoring the half of the data collected in the 6.4-keV channel.

Beginning in August 2004, raw data acquired by the Mössbauer spectrometers on the Mars Exploration Rovers (MERs) have been released to the science community as experimental data records (EDRs) for each Martian day (sol) on which measurements were made. To provide convenient direct access to the EDRs, to enable independent assessment and analysis, and to allow confirmation of MER-team scientific conclusions, a new Windows-based computer program, MERView, has been developed (Agresti et al. 2005a,b). Correction for nonlinearity is done using the EDR-provided drive error signal, a phase shift, and the requirement that the two halves of a reference spectrum must overlap exactly when plotted on a correct velocity scale defined relative to the maximum drive velocity ($V_{\text{max}}$). Converting the scale from %$V_{\text{max}}$ to mm/s is less straightforward.

Each of the MERs has a unique reference target used for calibration purposes, so that a reference spectrum can be acquired at the same time as each spectrum of a surface sample. The reference samples on the MERs consist of a mixture of $\alpha$-Fe, hematite, and magnetite (Klingelhöfer & Squyres, personal communication, 2005), although the relative proportions of these components are unknown. Laboratory-acquired spectra of the reference targets at temperatures experienced on Mars would be desirable, but these data have not been released by the MER team. The reference spectra are extremely complicated, and the targets on the two rovers are quite different. In both cases, the overlap of the hematite and magnetite subspectra is too great to allow them to be used directly for calibration. In the reference spectra there are four peaks arising from $\alpha$-Fe that are relatively free of overlap with the hematite and magnetite subspectra (the other two peaks of the $\alpha$-Fe sextet cannot be clearly resolved). We are using these four peak locations (at roughly 5.32, −3.08, 0.84, and 3.08 mm/s) to provide the mm/s calibration. MER spectra that have been corrected for nonlinearity and calibrated using this method are available on the Mount Holyoke Web site at http://www.mtholyoke.edu/go/mars.

**ILEEMS**

ILEEMS is an exciting new technique that utilizes the low-energy electrons emitted by the nuclei in the sample [the lowest-energy (E < ∼15 eV) and shake-off electrons in Figure 3]. The geometry of the apparatus is shown in Figure 8c.
Because the energy of these electrons is so low, their origin within the sample lies at a depth of only a few nanometers. Therefore, this technique is ideally suited to the study of surface processes and alteration in iron-bearing materials. This technique has just recently been brought to bear on materials of geologic interest by DeGrave et al. (2005), who are finding that fine layers of hematite are present on the surfaces of several other iron oxides in amounts that cannot be detected by any other technique.

**INTERPRETATION OF MÖSSBAUER DATA**

**Mössbauer Lineshapes**

As discussed earlier, the intrinsic emission spectrum is a Lorentzian centered at $E_0$ with linewidth, $\Gamma_0$ (Figure 1). That is, the probability distribution of the energy, $E$, of emitted recoilless gamma photons is given by

$$L_S(E, v; E_0, \Gamma_0) = \left(\frac{\Gamma}{2\pi}\right) \frac{1}{(E - E_0 - E_0v/c)^2 + (\Gamma_0/2)^2},$$

(6)

where the source is assumed to be moving with relative velocity, $v$, so that, by Equation 1, the center of the spectrum is Doppler shifted to $E_0 + E_0v/c$. A single-line, i.e., unsplit, absorption spectrum has in principle also a Lorentzian lineshape, but with fixed center at $E_0 + \text{IS}$, where $E_0 \gg \text{IS}$ (cf. Figure 4, red, and Figure 5, blue). It is thus of the form $L_A(E; E_0 + \text{IS}, \Gamma_A)$, where the velocity variable, $v$, has been omitted and the absorption linewidth is $\Gamma_A \neq \Gamma_0$, as might be the case if values for IS were distributed while preserving the Lorentzian lineshape.

As seen in Figure 4 (blue), the transmission spectrum dips from the baseline because resonant absorption of incident gamma photons changes as $v$ is varied. For “thin” absorbers where the Compton-corrected absorption (see earlier) is no more than 5%–10% depending on the precision required, Margulies & Ehrman (1961), showed that the resonant absorption is given by the overlap integral,

$$\int_{-\infty}^{+\infty} L_S(E, v; E_0, \Gamma_0) \cdot L_A(E; E_0 + \text{IS}, \Gamma_A) dE = L_A(v; \text{IS}, \Gamma_0 + \Gamma_A),$$

(7)

which is a Lorentzian function of $v$ centered at IS with linewidth $\Gamma_0 + \Gamma_A$, where the latter two quantities are now expressed in velocity units.

If the absorption spectrum is more complex (Figure 5, red and green), in the thin absorber limit it is then simply a sum of Lorentzians, and $L_A(\ldots)$ in Equation 7 is replaced by a weighted sum over functions, $L_A(E; E_0 + \text{IS}, \Gamma_i)$, where $\Gamma_i$ and $\Gamma_j$ refer to the individual absorption transitions. The transmission spectrum can then be modeled as a baseline minus a sum, or superposition, of Lorentzian “lines” with different positions, linewidths, and intensities (or areas). Note that these line properties are generally not independent of each other, as shown in Figure 5, where line positions are given by the Mössbauer parameters, IS, QS, and $B_{\text{dd}}$ for each distinct Fe nuclear site, linewidths are equal, and intensities are in the ratio of 1:1 or 3:2:1:1:2:3. Peak properties are defined by the Mössbauer parameters and other correlations, and not the other way around!
When the thin absorber limit is exceeded, special care must be exercised in modeling the transmission, as it is no longer a superposition of Lorentzians. Ideally, a “transmission integral” is computed that accounts for “saturation” of the resonance absorption that occurs for “thick” absorbers, which tends to flatten, or round, the deeper portions of the spectrum, increasing effective linewidths and distorting spectral areas. Why does such saturation occur? If $\mu(v)$ is the resonant absorption probability per unit thickness and $t_A$ the thickness, then transmission $I(v) = I_0 \exp[-\mu(v) t_A]$. For thin absorbers, $I(v) \sim I_0 - I_0 \mu(v) t_A$, and the absorption is proportional to $\mu(v)$ at all velocities, so no distortion occurs. For larger $t_A$, this approximation works for smaller $\mu(v)$, but not larger $\mu(v)$, which then lie on the rounded portion of the exponential, leading to less transmission than if the linear approximation were still valid at that velocity.

The transmission integral was derived for a single-line absorber by Margulies & Ehrman (1961) and for hyperfine splitting of the emission and absorption lines by Margulies et al. (1963). Because of its complexity and the time required to compute the integral repeatedly at each step in an iterative least-squares fitting routine, workarounds are typically employed, such as various corrections for saturation or use of lineshapes that are more rounded than the Lorentzian. With such approximations, precision in the Mössbauer parameters is somewhat compromised, and relative areas more so.

If several species of iron (i.e., different coordination states, coordination environments, etc.) contribute to a spectrum, then the total area of all the Lorentzian lines for each species is directly proportional to the number of atoms of that species. In the simplest analysis, relative site populations are determined by finding areas ratios. More precisely, the areas are proportional to the “true” populations by the following formulation (Preston et al. 1962, Bancroft 1967, 1969):

$$\frac{A_1}{A_2} = C \frac{n_1}{n_2} \quad \text{where} \quad C = \frac{\Gamma_1 f_1 G(X_1)}{\Gamma_2 f_2 G(X_2)}$$

(8)

and $G(X)$ is a saturation factor that depends, in part, on the thickness.

To put this in mineralogical terms, consider a simple example where two minerals (olivine and pyroxene) each have only $\text{Fe}^{2+}$ in octahedral coordination. The doublets corresponding to $\text{Fe}^{2+}_{\text{ol}}$ and $\text{Fe}^{2+}_{\text{px}}$ have areas equal to $A_1^{\text{ol}}$ and $A_1^{\text{px}}$, $n$ is the true amount of each species and $C$ is the correction factor. Using the formulation given above, we find that

$$\frac{A_1^{\text{ol}}}{A_1^{\text{px}}} = C \frac{n_1^{\text{ol}}}{n_1^{\text{px}}} \quad \text{where} \quad C = \frac{\Gamma_{\text{ol}} f_{\text{ol}} G(X_{\text{ol}})}{\Gamma_{\text{px}} f_{\text{px}} G(X_{\text{px}})}$$

(9)

Thus, to determine true site and valence state information from a Mössbauer spectrum from the Martian surface (or from a terrestrial laboratory) it is necessary to consider three factors:

1. The equal linewidth ($\Gamma$) assumption is only reasonable in end members, but most fitting routines can allow linewidths to vary.
2. The saturation corrections for $G(X)$ can be avoided if thin absorbers are used. However, for the backscatter mode spectra acquired on the Martian surface, understanding the extent of variation of $G(X)$ will be a problem.
3. As noted above, recoil-free fractions depend greatly on site geometries and valence states, and thus different values of $f$ are likely in cases where two sites have radically different geometries. Whipple (1968) has suggested that variations in $C$ can influence the results of Mössbauer $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios in silicates by up to 30%; much of this error is due to variations in $f$. DeGrave & van Alboom (1991), who worked on oxides and oxyhydroxides, found that failure to consider effects of differential $f$ could lead to errors averaging 15% for $\text{Fe}^{3+}/\text{Fe}^{2+}$. Thus, quantitative determinations of $f$ are critical to obtaining useful site occupancies and valences states.

**Recoil-Free Fraction**

Given the preceding discussion, it should come as no surprise that one of the active areas of Mössbauer research on minerals is the determination of recoil-free fractions in a systematic way. There are at least four ways to evaluate differential recoil-free fraction. The first, somewhat brute force method is to measure the $\text{Fe}^{3+}/\text{Fe}^{2+}$ in a number of samples of a given mineral species using an independent technique (e.g., wet chemistry), and then to calculate a value for $C$ based on equations given in Bancroft (1969). This method was used by Bancroft & Brown (1975), who inferred an average value of $C = 0.98 \pm 0.04$ for biotite, and by Whipple (1968), who made some very careful comparisons between Mössbauer and wet chemical data. These correction factors apply only to the specific compositions used in these studies, and do not apply to measurements at temperatures other than 300 K.

A second way to determine $C$ is to calculate $f$ using Mössbauer single-crystal measurements, as described in Tennant et al. (1992) and Tennant (1992). In this technique, the relationship between the Mössbauer fraction and the mean squared displacement (MSD) tensor (cf. Equation 5) is used to derive the Mössbauer fraction from a set of single-crystal Mössbauer spectra. Although this method has been proven workable, in the words of Tennant (1992), “The disadvantages are the difficulties in obtaining a meaningful MSD tensor, and the (consequent) tedious nature of the experiment.”

The third and fourth approaches both model the lattice-vibrational spectrum of $^{57}\text{Fe}$ using the Debye approximation (e.g., Frauenfelder 1962, Goldanskii & Herber 1968). In the Debye approximation, the absorber is assumed to be isotropic and elastic. Its vibrations have a finite range of frequencies characterized by the Debye temperature, $\theta_D$, which is proportional to the maximum vibrational frequency of the lattice. All the directions of emission of phonons have equal probabilities. This model oversimplifies complex lattice systems, especially in the region of high frequencies (Goldanskii & Herber 1968), but as long as it is used in the comparison of structurally similar systems, it appears to be an adequate approximation (Eeckhout & DeGrave 2003). The third method determines $f$ by measuring the temperature dependence of peak areas and relating that back to $f$ by means of the thickness parameter (Lafleur & Goodman 1971).

A fourth approach to quantifying $f$ is to use the temperature dependence of the center shift (IS). Mössbauer spectra of the mineral of interest are acquired over a range
Recoil-free fraction ($f$): fraction of times a photon is emitted or absorbed without energy transfer to (or from) the host lattice in a Mössbauer transition, i.e., a transition that can exhibit the Mössbauer effect, such as the 14.4-keV ground to first-excited state transition in $^{57}$Fe.

The temperature dependence of the center shift is fit to the Debye integral approximation to determine a value for $\theta_D$ and $\delta_I$ using

$$ IS(T) = \delta_I - \frac{9}{2} \frac{k_B T}{M c} \left( \frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1}, $$

where $\delta_I$ is the intrinsic isomer shift, $M$ is the mass of the Mössbauer nucleus, and $\theta_D$ is referred to as the characteristic Mössbauer temperature, $\theta_M$ (DeGrave et al. 1985).

A large value for $\theta_M$ suggests a “stiff” lattice.

Next, the fitted value for $\theta_D$ is used in the Debye integral approximation for the recoil-free fraction to calculate $f(T)$ for each site using the relation:

$$ f(T) = \exp \left[ -\frac{3}{2} \frac{E_R}{k_B \theta_D} + \left[ 1 + 4 \left( \frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{xdx}{e^x - 1} \right] \right]. $$

(11)

Note from this expression that when $\theta_D$ is large, $f$ will be large. Thus, higher values of $f$ are indicative of more tightly bound atoms.

Further information on this method can be found in Herberle (1971), Grant (1995), and DeGrave et al. (1985). Such determinations of the recoil-free fractions for $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ in assorted minerals by DeGrave & van Alboom (1991) and Eeckhout & DeGrave (2003) have shown that $f$ values are strongly mineral, site, and composition dependent. Rancourt (1994) found that recoil-free fractions were equal for all sites in a synthetic annite within experimental error. A related thesis by Royer (1991) made a detailed study of site-specific recoil-free fractions in Fe-bearing trioctahedral micas and apparently found larger $f$ values for $\text{Fe}^{3+}$ in micas than for $\text{Fe}^{2+}$ (as reported in Rancourt 1994). The overview paper by Eeckhout & DeGrave (2003) summarizes most of the known $f$ values for minerals. Characterization of $f$ values for common rock-forming minerals is ongoing in our research group (Rothstein et al. 2005, Sklute et al. 2005). Values for $f$ typically range from 0.65 to 1.

It is worth noting that values of $f$ determined by this method rely on a somewhat unrealistic approximation of the Debye model, and the calculated $\theta_M$ has little physical meaning. However, $f$ values determined in this way do have value as phenomenological parameters, and they do allow comparison of different lattice sites within a given compound or in the comparison of structurally related compounds (DeGrave & van Alboom 1991). Some ground-truth comparisons of $f$ values have been made using this method. DeGrave & van Alboom (1991) acquired Mössbauer spectra of binary mixtures made with known relative contents of different minerals (hematite, goethite, lepidocrocite, ilmenite, and ferrochromite) and compared the resultant peak areas with $f$ values determined using the method just described. The agreement between calculation and experiment was within 0.035 or closer. However, for some purposes, additional measurements of mixed minerals may be desirable.

Fitting Mössbauer Data

Techniques for processing Mössbauer data are complex and variable. There are at least four popular 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 (e.g., Rancourt 1994, Lagarec & Rancourt 1997). In Rancourt (1994), fitting with Lorentzian line doublets was compared to fitting with quadrupole splitting distributions (using the Recoil program). In the quadrupole splitting distribution model (as in the hyperfine field distribution model for magnetically split spectra), any broadening of the absorption lines beyond their intrinsic linewidth is assumed to be due to a Gaussian distribution of static hyperfine parameters, producing Voigt-shaped lines (Rancourt & Ping 1991).

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.

There are at least four most commonly used, easily available computer programs. These include WMOSS, from WEB Research Co. in Minnesota (http://www.webres.com, originally commercial, but recently released to the public domain); Recoil, from the University of Ottawa, in Canada (http://www.physics.uottawa.ca/~recoil/, a commercial product); MossWinn, from Loránd Eötvös University, in Hungary (http://www.mosswinn.com, a commercial product); and an in-house suite of programs from the University of Ghent, in Belgium (referred to here as the Ghent programs). WMOSS is capable of assuming seven different physical models in its fitting, including quadrupole splitting distributions with Voigt-based fitting and hyperfine field distributions with Voigt-based fitting. It can use any of five different fitting algorithms. Recoil may assume all these models, as well as several others, and is capable of calculating full Hamiltonians. MossWinn (Klencsár et al. 1998) uses pseudo-Voigt functions and calculates an exact solution of the nuclear Hamiltonian, although it, too, calculates the quadrupole splitting distribution and hyperfine field distribution. The Ghent programs [based on Wivel & Morup (1981)] can use discrete quadrupole splittings or distributions, discrete hyperfine fields, or distributions, with Lorentzian lineshapes and the capability of correlating isomer shifts with quadrupole splitting or hyperfine field distributions. In addition, they also have the capability of calculating full Hamiltonians.

Preliminary results of our ongoing study to compare these four programs highlight the necessity for intelligent and thoughtful fitting of Mössbauer spectra (Schaefer & Dyar 2005). It is possible to produce fits of a single, relatively simple spectrum that have similar chi-squared values but significantly different Mössbauer parameters or even numbers of peaks. Initial estimates of peak parameters and use of constraints can
have dramatic effects on fits. Results can be highly variable, not only between programs but also while fitting with one program alone. Clearly more work must be done to determine the causes of this variability and the best methods of interpreting these results. This is important not just to the interpretation of present and future spectra, but to the understanding of spectra and Mössbauer parameters in the literature.

Other Constraints

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.

NEW DIRECTIONS

In recent years, the fields of mineralogy, geochemistry, and petrology have become more dependent on microanalytical techniques. The recent improvements in instrumentation for and modeling of Mössbauer spectra have opened up possibilities for analysis of a much broader range of materials than ever before because low-Fe materials and small sample quantities can now be studied successfully. These advances are expected to turn the interest of the scientific community once again to the study of $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ partitioning in a wide variety of geological materials.

Three examples of applications of Mössbauer spectroscopy serve to illustrate these advances. The first involves the study of Fe in feldspar, which is the most common mineral group in Earth’s crust. Because feldspar is so low in Fe, it has not been studied with Mössbauer spectroscopy since the 1970s-era papers on Apollo lunar samples, but new spectrometers can easily analyze feldspar, and even discriminate between Fe in feldspar and Fe in oxide inclusions. We are currently studying the valence state of iron in plagioclase within the Pyroxenite Marker (PM) magma influx in the Bushveld Complex (Lundgaard 2003). The FeO$_{\text{Total}}$ contents of plagioclase increases systematically within the 400-m-thick mixing zone below the PM at Roossenekal from 0.39 wt% at −383 m to 0.63 wt% at −6 m, followed by an abrupt decrease to 0.48 wt% 25 m above the PM. This overall increase in FeO$_{\text{Total}}$ of the plagioclases across the PM is opposite to the coexisting orthopyroxenes that show iron depletion. One explanation for this apparent discrepancy is that the new magma added had higher FeO$_{\text{Total}}$ and Mg-number than the resident magma. Another interpretation of the increase in FeO$_{\text{Total}}$ of plagioclase is that the new magma had higher oxygen fugacity, which would be reflected in plagioclase Fe$^{3+}$/ΣFe contents. To evaluate these hypotheses, we have acquired Mössbauer spectra on plagioclase separates (Figure 9);
Room-temperature Mössbauer spectrum of feldspar from the Bushveld Complex. Although this sample has <0.1 wt% FeO, data of the quality shown here have been consistently acquired with use of a hot source, large sample size, and long run time along with modern instrumentation.

these data demonstrate that it is possible to obtain high-quality Mössbauer data even on samples with very low Fe contents. Mössbauer determinations of Fe$^{3+}$/ΣFe of plagioclase separates from the Rooseneekal profiles are providing direct constraints on the changes in oxygen fugacity of the magmas from which the PM cumulate sequence crystallized.

The lead author has long been collaborating with Charles Guidotti at the University of Maine to study the chemistry of western Maine metapelites within a petrologic framework. Our joint studies have focused on the changes in Fe valence and site occupancy in minerals over a range of temperatures and $f_0_2$ conditions. We are working with a well-characterized suite of metapelites from lower garnet zone up to K-feldspar + sillimanite zone conditions with a range of mineral assemblages representing $f_0_2$, from graphite/ilmenite to magnetite-hematite-bearing rocks. To date, we have studied biotite (Guidotti & Dyar 1991), staurolite (Dyar et al. 2002), and muscovite (Guidotti et al. 1994) in these rocks, but Mössbauer analysis of chlorites from Guidotti et al. (1994) has long been stymied by the difficulty of obtaining large quantities of pure mineral separates. The task of handpicking the fine-grained chlorites from these rocks (at a rate of approximately 1 mg/h) made it difficult to get the 200 mg of sample previously needed to obtain good quality Mössbauer data. Although the old samples were too small in mass to give good results in 1991, their 7–30 mg masses are now more than sufficient to obtain excellent quality Mössbauer data with current instrumentation. A spectrum of a 7 mg chlorite is shown in Figure 10. Preliminary data from samples in this suite suggest that chlorite contains roughly 25% of the total Fe as Fe$^{3+}$, independent of metamorphic grade. Further work will evaluate the effect of changing oxide assemblage on Fe$^{3+}$ in chlorite. This study illustrates the current capability of Mössbauer spectroscopy to study samples that can be easily handpicked.
Figure 10
Room-temperature Mössbauer spectrum of chlorite from western Maine. The sample was fit using quadrupole splitting distributions; the figure shows three Fe$^{2+}$ subcomponents (blue) and two Fe$^{3+}$ components (red), along with a minor ilmenite impurity (orange). The sum of the fitted components is shown in green. This chlorite was handpicked from a fine-grained metamorphic rock; the mount contained 7 mg of sample.

A final example of innovative use of MS can be shown using a comparison of ILEEMS (which makes measurements at a few-nanometer depths) and conventional transmission data on hematite, α-Fe$_2$O$_3$, as described in DeGrave et al. (2005). To explain this example, it is necessary to understand the magnetic characteristics of hematite. At temperatures above $\sim$265 K (for the pure, well-crystalline endmember), hematite is a weak ferromagnet (WF). Electron spins in adjacent sites will align nearly perpendicular to the $c$ axis, with a small canting along that axis. The weak ferromagnetism is a result of the summing of the spin components along the $c$ axis, all of which are parallel to each other. As a result, hematite takes on its own weak magnetization.

Below $\sim$265 K, Fe$^{3+}$ atoms in adjacent sites have exactly equal and opposite magnetic moments. In this case, the moments cancel out perfectly, and the material will have no magnetic moment. The atomic magnetic moment changes direction to become parallel to the $c$ axis (spin flop), and the hematite becomes an antiferromagnet (AF). In hematite, this change is usually designated as the Morin transition, $T_M$ (Morin 1950, Morrish 1994).

Variable temperature measurements by MS can be used to distinguish between the ferromagnetic and AF states because each gives rise to a sextet with its own distinctive hyperfine field and quadrupole splitting. Such studies have been used to show that $T_M$ decreases in hematites with small particle sizes and poorer crystallinities, and that substitution of other elements such as Al for Fe$^{3+}$ also lowers $T_M$ (see, e.g., DeGrave et al. 1988). At temperatures close to $T_M$, contributions from both the WF and the AF spin states are present in Mössbauer spectra. DeGrave et al. (1988) suggested that such coexisting spin states might be explained if the surfaces of the hematite particles undergo the Morin transition at a different temperature than the interiors of the...
crystals. Subsequent work (Vandenberge et al. 2001) has suggested that intermediate spin states might occur as part of the spin flop.

To address this issue, DeGrave et al. (2005) collected ILEEMS and conventional Mössbauer spectra of two hematites: one with the endmember $\alpha$-$\text{Fe}_2\text{O}_3$ composition and one with a small amount of Al substitution for Fe ($\alpha$-$\text{Fe}_{1.87}\text{Al}_{0.13}\text{O}_3$). As shown in Figure 11, each spectrum has been fitted with two sextets corresponding to the

![Mössbauer spectra of hematite, $\alpha$-$\text{Fe}_2\text{O}_3$ (left top and bottom) and Al-substituted hematite, $\alpha$-$\text{Fe}_{0.935}\text{Al}_{0.065}\text{O}_3$ (right top and bottom) acquired using the surface technique of ILEEMS (top set, emission) and conventional transmission Mössbauer, which samples the bulk mineral.](image)

**Figure 11**
Mössbauer spectra of hematite, $\alpha$-$\text{Fe}_2\text{O}_3$ (left top and bottom) and Al-substituted hematite, $\alpha$-$\text{Fe}_{0.935}\text{Al}_{0.065}\text{O}_3$ (right top and bottom) acquired using the surface technique of ILEEMS (top set, emission) and conventional transmission Mössbauer, which samples the bulk mineral. Adapted from figure 8 in DeGrave et al. (2005). Only the positive velocity half of each spectrum is shown for simplicity. Each spectrum contains two sextets: one corresponding to an antiferromagnetic (AF, shaded blue, $T < T_M, QS > 0$) spin state, and one to a weakly ferromagnetic state (WF, $T > T_M, QS < 0$). In the pure hematite, the spectrum of the surface is nearly the same as the bulk sample; both contain comparable amounts of WF and AF iron. In the Al-substituted sample, the WF sextet dominates the ILEEMS (surface emission) measurement, indicating that the bulk of the Fe at the surface is already above the Morin transition. In the bulk transmission measurement of the same sample, the WF and AF sextets are of similar areas. There appear to be two values for $T_M$ in the sample, roughly half of the sample having one value, the other half another value. The temperature of the sample lies between these two values.
WF (unshaded red lines, $QS < 0$) and the AF (shaded blue lines, $QS > 0$) contributions. In the pure (albeit small crystalline) hematite, the spectrum of the surface is roughly the same as the bulk sample; both contain comparable amounts of WF and AF iron, with WF somewhat enhanced in the surface as compared with the bulk sample.

In the Al-substituted sample, the emission and transmission spectra are dramatically different. In the surface (ILEEMS) measurement, the WF sextet (red) is far more intense than the AF sextet (shaded blue), while in the transmission data, both sextets are again comparable in intensity. These and related measurements at varying temperatures suggest that $T_M$ is significantly lowered in the top monolayers of the hematites. One partial interpretation of this result is that the surface layers may be richer in Al than the interiors (DeGrave et al. 2005); work is ongoing in that research group to further explore these results. This study exemplifies the potential of surface Mössbauer measurements to add greatly to our understanding of redox processes that occur in the outermost layers of minerals.

**PREPARING FOR THE NEXT 50 YEARS**

To prepare this field for important geological studies over the next 50 years (and beyond!), two important issues need to continue to be addressed. The first is the determination of the fundamental Mössbauer parameters of commonly occurring rock-forming minerals: the intrinsic isomer shift, $\delta_I$, the characteristic Mössbauer temperature, $\theta_M$, and the recoil-free fraction, $f$. These factors are analogous to matrix-correction effects utilized in electron microscopy in that they are used to convert peak area ratios determined spectroscopically into valid estimates of actual species concentrations. Robust application of Mössbauer spectroscopy to geoscience problems will require that these parameters be known over a broad compositional range in the major rock-forming mineral groups.

The second task follows from the first: The need to evaluate current physical models and computer algorithms for fitting Mössbauer data, and to compare their results to true valence state and site occupancies as determined by wet chemistry and single crystal X-ray diffraction, respectively. Variations in results from fitting procedures among different laboratories are as yet largely undocumented, although our preliminary work suggests significant discrepancies in spectral parameters determined from the commonly employed fitting routines. Mössbauer spectroscopists need to be able to reliably compare results from different research groups, and also to make informed choices for using software that is most appropriate for their data.

By addressing these issues, we will effectively reduce the error bars on studies of Fe using Mössbauer spectroscopy, increase understanding of fitting models and algorithms, and expand the application of Mössbauer spectroscopy to an even larger range of studies of geologic materials.
SUMMARY POINTS

1. Since the early 1960s, Mössbauer spectroscopy in the geosciences has been predominantly used to study the valence state and coordination of Fe atoms.

2. Mössbauer spectroscopy is based on the concept of resonant absorption of nuclear gamma-rays in solids.

3. Mössbauer parameters include isomer shift (IS), which reflects the $s$-electronic charge density at the nucleus; quadrupole splitting (QS), which arises from a distribution of surrounding charges with less than cubic symmetry; and the magnetic hyperfine field ($B_{hf}$), which indicates magnetic order or an externally applied field.

4. IS, QS, and $B_{hf}$ vary fairly systematically with the valence state ($Fe^0$, $Fe^{2+}$, $Fe^{3+}$) and coordination number (generally 4- to 8-coordination) of Fe. Because rules for atomic radius ratios predict that $Fe^{3+}$ will most commonly occur in 4- or 6-coordination with oxygen, and $Fe^{2+}$ in 6-coordination, many minerals have the same or quite similar Mössbauer parameters. Thus, Mössbauer parameters are generally not sufficiently diagnostic for mineral identification.

5. Mössbauer instrumentation now includes many variations, such as transmission, backscatter, milliprobe, CEMS, and integral low-energy electron Mössbauer spectroscopy (ILEEMS). The technique is now routinely used for the study of very small Fe-rich geological samples (1–10 mg), as well as larger amounts of low-Fe samples such as feldspar.

6. Interpretation of Mössbauer lineshapes is quite complex, and software available for analysis uses a variety of physical models. Fits using different models may produce highly variable results.

7. Recoil-free fraction ($f$), which is a measure of the rigidity of the bonds surrounding the Fe atom, is the most important factor that must be known to relate the peak areas in a Mössbauer spectrum to the actual abundances of the represented species.

8. Future work in this field must address the variation of $f$ with mineral composition and structure and resolve differences in interpretation that arise from use of different fitting models.

ACKNOWLEDGMENTS

This work was supported by NASA grants NAG5-12687 and NNG04GG12G and NSF grants EAR-0439161 and EAR-0439077. We thank Tom Kent for contributions to the instrumentation section; Kylie Hanify and Yarrow Rothstein for help with citations; and Eddy DeGrave for preprints, thoughtful discussions, and use of figures from works in progress.
LITERATURE CITED


Bancroft GM. 1969. Quantitative site populations in silicate minerals by the Mössbauer effect. Chem. Geol. 5:255–58


Thorough (although slightly outdated) coverage of the application of Mössbauer spectroscopy to the study of minerals, with many examples of rock-forming minerals.
Barbier J, Grew ES, Halenius E, Halenius U, Yates MG. 2002. The role of Fe and cation order in the crystal chemistry of surinamite, \((\text{Mg,Fe}^{2+})_3(\text{Al,Fe}^{3+})_3\text{O}[\text{AlBeSi}_3\text{O}_{15}]\): a crystal structure, Mössbauer spectroscopic, and optical spectroscopic study. *Am. Mineral.* 87:501–13


Describes the relationships between Mössbauer parameters and the geometry and distortion of the coordination polyhedra occupied by Fe atoms. It uses unusual mineral structures to probe the ranges of IS and QS for different coordination numbers for Fe\(^{2+}\) and Fe\(^{3+}\).

First summary paper describing the prevailing method of approximating recoil–free fractions in minerals. It presents data on a large number of minerals, with emphasis on Fe oxides.

Explanation of the new technique of ILEEMS, and its potential application to the study of mineral surfaces.


A careful discussion of the Mössbauer instrumentation included on the Mars Exploration Rovers.
Description of application of Voigt-based methods to interpretation of Mössbauer data, providing background information for commonly used fitting routines.


Vogel RH, Evans BJ. 1980. $^{57}$Fe Mössbauer study of the crystal chemistry of strunzite, MnFe$_2$PO$_4$·(OH)$_2$·6H$_2$O. *J. Phys. Coll.*, 41:297–98


Contents

Threads: A Life in Geochemistry
  Karl K. Turekian ................................................................. 1

Reflections on the Conception, Birth, and Childhood of Numerical Weather Prediction
  Edward N. Lorenz .............................................................. 37

Binary Minor Planets
  Derek C. Richardson and Kevin J. Walsh ................................. 47

Mössbauer Spectroscopy of Earth and Planetary Materials
  M. Darby Dyar, David G. Agresti, Martha W. Schaefer, Christopher A. Grant, and Elizabeth C. Sklute .......................................................................................................................... 83

Phanerozoic Biodiversity Mass Extinctions
  Richard K. Bambach .............................................................. 127

The Yarkovsky and YORP Effects: Implications for Asteroid Dynamics
  William F. Bottke, Jr., David Vokrouhlický, David P. Rubincam, and David Nesvorný .......................................................... 157

Planetesimals to Brown Dwarfs: What is a Planet?
  Gibor Basri and Michael E. Brown ........................................... 193

History and Applications of Mass-Independent Isotope Effects
  Mark H. Thiemens ................................................................. 217

Seismic Triggering of Eruptions in the Far Field: Volcanoes and Geysers
  Michael Manga and Emily Brodsky .......................................... 263

Dynamics of Lake Eruptions and Possible Ocean Eruptions
  Youxue Zhang and George W. Kling ........................................ 293

Bed Material Transport and the Morphology of Alluvial River Channels
  Michael Church ......................................................................... 325

Explaining the Cambrian “Explosion” of Animals
  Charles R. Marshall .................................................................. 355
Cosmic Dust Collection in Aerogel
Mark J. Burchell, Giles Graham, and Anton Kearsley ........................................... 385

Using Thermochronology to Understand Orogenic Erosion
Peter W. Reiners and Mark T. Brandon ................................................................. 419

High-Mg Andesites in the Setouchi Volcanic Belt, Southwestern Japan:
Analogy to Archean Magmatism and Continental Crust Formation?
Yoshiyuki Tatsumi .................................................................................................. 467

Hydrogen Isotopic (D/H) Composition of Organic Matter During
Diagenesis and Thermal Maturation
Arndt Schimmelmann, Alex L. Sessions, and Maria Mastalerz ............................... 501

The Importance of Secondary Cratering to Age Constraints on
Planetary Surfaces
Alfred S. McEwen and Edward B. Bierhaus ......................................................... 535

Dates and Rates: Temporal Resolution in the Deep Time Stratigraphic
Record
Douglas H. Erwin .............................................................................................. 569

Evidence for Aseismic Deformation Rate Changes Prior to
Earthquakes
Evelyn A. Roeloffs .......................................................................................... 591

Water, Melting, and the Deep Earth H2O Cycle
Marc M. Hirschmann ....................................................................................... 629

The General Circulation of the Atmosphere
Tapio Schneider ............................................................................................. 655

INDEXES

Subject Index ....................................................................................................... 689
Cumulative Index of Contributing Authors, Volumes 24–34 ....................... 707
Cumulative Index of Chapter Titles, Volumes 24–34 .................................... 710

ERRATA

An online log of corrections to Annual Review of Earth and Planetary Sciences
chapters may be found at http://earth.annualreviews.org