



Ferric iron in SNC meteorites as determined by Mössbauer spectroscopy: Implications for martian landers and martian oxygen fugacity

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Abstract—Mössbauer spectra of martian meteorites are currently of great interest due to the Mössbauer spectrometers on the Athena mission MER rovers as well as the European Space Agency Mars Express mission, with its Beagle 2 payload. Also, considerable current effort is being made to understand the oxygen fugacity of martian magmas because of the effect of fO_2 on mineral chemistry and crystallization processes. For these 2 reasons, the present study was conceived to acquire room temperature Mössbauer spectra of mineral separates and whole rock samples of 10 SNC meteorites. The results suggest that mineral identification using remote application of this technique will be most useful when the phases present have distinctive parameters arising from Fe in very different coordination polyhedra; for example, pyroxene coexisting with olivine can be discriminated easily, but opx versus cpx cannot. The MER goal of using Mössbauer spectroscopy to quantify the relative amounts of individual mineral species present will be difficult to satisfy if silicates are present because the lack of constraints on wt% FeO contents of individual silicate phases present will make modal calculations impossible. The remote Mössbauer spectroscopy will be most advantageous if the rocks analyzed are predominantly oxides with known stoichiometries, though these phases are not present in the SNCs. As for the detection of martian oxygen fugacity, no evidence exists in the SNC samples studied of a relationship between Fe^{3+} content and fO_2 as calculated by independent methods. Possibly, all of the Fe^{3+} observed in olivine is the result of dehydrogenation rather than oxidation, and this process may also be the source of all the Fe^{3+} observed in pyroxene. The observed Fe^{3+} in pyroxene also likely records an equilibrium between pyroxene and melt at such low fO_2 that little or no Fe^{3+} would be expected.

INTRODUCTION

With the inclusion of Mössbauer spectrometers in the instrument payloads of both MER landers in the upcoming Athena mission, as well as the Beagle 2 payload of the European Space Agency mission to Mars, attention will be focused on Mössbauer spectra of martian meteorites. However, these data are widely scattered in the literature, mostly in the form of abstracts. Data have been acquired at different scales and temperatures, making comparisons among different studies difficult, and only 3 spectra of mineral separates from SNC (martian) meteorites, which are needed to understand the relationship between individual mineral chemistry and bulk rock characteristics, have been published. None of the published spectra has been acquired at temperatures analogous to those on the martian surface, and recoil-free fraction effects for the phases in SNC meteorites are poorly known. This paper represents the first in a series of

publications on SNC Mössbauer spectra in which the majority of fallen and Antarctic meteorites are studied both as bulk samples and as mineral separates, using a single high sensitivity spectrometer over a variable temperature range. This endeavor is of critical importance in preparing to interpret MER, Beagle 2, and other remotely-acquired Mössbauer spectra from the martian surface.

In addition to spectral characterization and interpretation, a second aspect of this study is important. Knowledge of oxygen fugacity is of paramount importance in constraining phase equilibria and crystallization processes of melts, as well as understanding the partitioning of elements between the core and silicate portions of terrestrial planets. Several ways of estimating the oxygen fugacity of Mars based on the SNC meteorites are available, including use of Fe-Ti oxides (Herd et al. 2001), olivine-pyroxene-spinel barometry (Herd 2002; Herd et al. 2002), Eu oxybarometry (McCanta and Rutherford 2002; Musselwhite and Wadhwa 2002; Wadhwa 2001), and

$\text{Fe}^{3+}/\Sigma\text{Fe}$ by XANES (Delaney and Dyar 2000; Delaney et al. 1998a), or Mössbauer. However, the relationship between the reported Fe^{3+} values and the other methods for estimating $f\text{O}_2$ is not clear, and further measurements of $\text{Fe}^{3+}/\Sigma\text{Fe}$ by a more conventional technique have been needed.

In the present study, Mössbauer spectra are acquired from mineral separates picked from SNC meteorites, as well as of the whole rocks from which the separates were prepared. With these data, both the interpretation of remote martian Mössbauer spectra and the relationship between SNC Fe^{3+} contents and $f\text{O}_2$ can be discussed, as these are very much interrelated. Thus, this paper addresses the following issues:

1. As a group, what do the whole rock Mössbauer spectra of SNC meteorites predict for possible Mössbauer spectra acquired on the martian surface?
2. How are the whole rock spectra related to the spectra of mineral separates, and what can be learned from whole rock spectra about the Fe^{3+} composition and identities of individual minerals?
3. How are the Fe^{3+} contents of the minerals in the SNCs related to the oxygen fugacity of the magmas from which they formed?

SNC METEORITES

The informal term “SNC” has been adopted as the abbreviation for the group of meteorites classified as shergottites, nakhlites, or chassignites, based on the type specimen for each group: meteorites from Shergotty, Nakhla, and Chassigny. This group of samples, which currently comprises 29 samples, is linked by similarities in age, bulk composition, and petrology. They are all mafic igneous rocks produced by volcanism, and they reflect analogous processes of melting, differentiation, and crystallization to those found on Earth. Their martian origins were confirmed by the evidence of Bogard and Johnson (1983) and Bogard et al. (1984), who found that trapped noble gases in EET A79001 were nearly identical to the martian atmosphere that had been measured by the earlier Viking landers, as well as by a number of lines of indirect evidence (e.g., their youth reflects a large source body with recent volcanism, cf., Wood and Ashwal [1981], and they are isotopically distinct from all other meteorites and from Earth [Clayton and Mayeda 1983]).

In this study, 11 lithologies from 10 SNC meteorites are studied (Table 2). This effort was focused on relatively-pristine Antarctic meteorites so that effects of terrestrial alteration might be somewhat mitigated. For this reason, no desert finds were considered except Los Angeles (which posed some serious problems for interpretation; see below). The samples studied are largely composed of pyroxene, glass, feldspar (or its shock-melted equivalent, maskelynite), and olivine, as tabulated in Table 2. Because feldspar/maskelynite does not contain enough Fe to contribute significantly to a Mössbauer spectrum, it was not studied here. Also, obtaining

a clean separate of glass only was not possible. Thus, efforts were focused on obtaining spectra of the major Fe-bearing silicates present in each meteorite in amounts greater than roughly 5% of the mineral mode. These included olivine, orthopyroxene, and clinopyroxene in varying amounts depending on the meteorite studied.

Representatives of each of the main lithologies for SNC meteorites were considered. Nakhla is an olivine-bearing clinopyroxenite. Shergotty, Zagami, EET A79001,B, QUE 94201, and Los Angeles are all basaltic shergottites, and they consist primarily of plagioclase, pigeonite, and augite, with the addition of Fe-Ti oxides. ALH A77005 and LEW 88516 are lherzolitic shergottites, with coarser grain sizes than the other shergottites; they are predominantly olivine with lesser amounts of orthopyroxene. EET A79001,A is an olivine-pyrrhotite shergottite (Goodrich 2002). Chassigny is a dunite with >90 modal% olivine (Prinz et al. 1974) and small amounts of clinopyroxene, and ALH 84001 is an orthopyroxenite that contains at least 97 modal% orthopyroxene (Harvey and McSween 1994). An excellent summary of data on the SNC meteorites is given in McSween (1985) and in the Mars Meteorite Compendium (Meyer 2003).

PREVIOUS WORK

Previous Mössbauer studies of SNC meteorites are summarized in Table 1. Much of the work in this field was done by Roger Burns and students; his interest was primarily in understanding the extent to which Fe^{3+} in these meteorites was related to possible weathering, either by low-temperature reactions on the martian surface or post-terrestrial ones in Antarctica.

The only workers to extract and analyze mineral separates were Ostertag et al. (1983), Ostertag et al. (1984; olivine), Vieira et al. (1986), and Vistisen et al. (1990) (pyroxene). The olivines in ALH A77005 display a unique brown-yellow color, which was attributed by Ostertag et al. (1984) to be pre-terrestrial and probably shock-induced. Burns (1989) later disputed the 4.5% Fe^{3+} observed by Ostertag et al. (1984) based on the absence of sextets attributable to magnetically ordered Fe^{3+} ions (that are typical in ferri-olivines and heat-induced olivines) in his 4.2 K spectra of whole rock ALH A77005. He suggested that there must be <2% Fe^{3+} and noted that the discrepancy might be attributed to magnetic dilution of structural Fe^{3+} ions or to nanocrystallinity of Fe^{3+} oxide intergrowths (Burns 1989).

Data of Vieira et al. (1986) demonstrated the presence of a small amount of magnetic phase in Zagami that was not magnetite and suggested that it might be pyrrhotite. This is puzzling given the petrographic studies of Stolper and McSween (1979), which found only 0.2–0.5% of the mode to be pyrrhotite and 2.1–2.2% to be titanomagnetite. Perhaps the aliquot studied by Vieira et al. was unusual in that it lacked titanomagnetite. Vieira et al. (1986) found only Fe^{2+} pyroxene peaks in their paramagnetic fractions from Zagami.

Table 1. Mössbauer spectroscopy of SNC samples.^a

Meteorite	Type	Analysis	References	%Fe ³⁺
ALH A77005	S	Whole rock	Burns 1989, 1991a, b; Burns and Solberg 1988; Solberg and Burns 1989	1.7–1.8
ALH A77005	S	Olivine	Ostertag et al. 1983, 1984	4.5
Chassigny	C	Whole rock	Burns 1991a, b; Burns and Martinez 1990a, b	2.3
EET A79001	S	Whole rock	Burns 1991a, b; Burns and Solberg 1988; Solberg and Burns 1989; Vieira et al. 1986	0.5–1.9
Governador Valadares	N	Whole rock	Burns 1991a, b	n.s.
Lafayette	N	Whole rock	Burns 1991a, b	n.s.
Nakhla	N	Whole rock	Agerkvist et al. 1994; Burns 1991a, b; Burns and Solberg 1988; Solberg and Burns 1989; Vieira et al. 1986	1.6
Nakhla	N	Paramagnetic and magnetic fractions	Vieira et al. 1986; Knudsen 1992	n.s.
Nakhla	N	Pyroxene	Vistisen et al. 1990	2.0
Shergotty	S	Whole rock	Burns 1991a, b	n.s.
Zagami	S	Whole rock	Agerkvist and Vistisen 1993; Agerkvist et al. 1994; Burns 1991a, b; Morris 1998; Vieira et al. 1986	n.s.
Zagami	S	Paramagnetic and magnetic fractions	Vieira et al. 1986; Knudsen 1992	trace

^an.s. = not specified; n.d. = not detected; S = shergottite, N = nakhlite; and C = chassignite.

 Table 2. Mineral modes (%) for samples studied.^a

Meteorite	Cpx	Opx	Fsp ^b	Ol	Ox	Sulf	Phos	Melt	Other ^c	Ref.
ALH A77005	3.7 ^d	9.5	9.5	60.2	2.6	0.3	0.4	13.7	n.r.	Lundberg et al. (1990); McSween et al. (1979); Treiman et al. (1994)
ALH 84001	n.r.	97	1	tr.	2	n.r.	0.15	n.r.	n.r.	Harvey and McSween (1994); Mason et al. (1992)
Chassigny	5 ^d	–	1.7	91.6	1.4	tr.	tr.	0.3	n.r.	Floran et al. (1978); Prinz et al. (1974)
EET A79001,A	65.4 ^d	5.4	17.1	8.9	3.1	–	0.4	–	0.3	Averages of McSween and Jarosewich (1983)
EET A79001,B	59.5 ^d	n.r.	29.1	n.r.	3.5	–	0.4	–	0.7	Averages of McSween and Jarosewich (1983)
LEW 88516	12–35 ^d	25.3	5–16	45.9–59	0.3–3	0.3	0.9–1.7	7.7	n.r.	Gleason et al. (1997); Treiman et al. (1994); Wadhwa et al. (1993)
Los Angeles	38–41.6 ^d	n.r.	43–53.9	1.9–4	1–3	0.7	1–3	n.r.	1.5	Mikouchi, (2001); Rubin et al. (2000); Xirouchakis et al. (2002)
Nakhla ^e	80	n.r.	n.r.	10	n.r.	n.r.	n.r.	n.r.	10	Friedman et al. (1994); Meyer (2003)
QUE 94201	44 ^d	n.r.	46	n.r.	2	n.r.	4	n.r.	4	Harvey et al. (1996)
Shergotty	67–70.5 ^d	n.r.	20–24	n.r.	2.2–8	0.2–0.4	tr.–2	n.r.	3.5–5.2	Smith and Hervig (1979); Stöffler et al. (1986); Stolper and McSween (1979)
ZagamiX ^f	69.7–80.4 ^d	n.r.	17.6–24.7	n.r.	1.5–2.8	0.2–.6	0.5–1.3	0.1–0.9	1.7–3.7	McCoy et al. (1992); Stolper and McSween (1979)

^an.r. = not reported; tr. = phase present in trace or minor amounts.

^bFsp or maskelynite.

^cOther = mesostasis or fusion crust.

^dBoth high-Ca and low-Ca clinopyroxene are present.

^eFriedman et al. (1994) found that the ratio of pyroxene to olivine varied from 4:1 to over 17:1 in 8 different samples of Nakhla; the major pyroxene in Nakhla is augite with some overgrowths of less calcic pyroxene (Harvey and McSween 1991; Treiman 1990).

^fDoes not include DN lithology (McCoy et al. 1993). Note also that Vistisen et al. (1992) reported large-scale heterogeneity of this meteorite; although they report as much as 23% modal olivine in one of their samples, our aliquot did not contain any olivine that could be detected by Mössbauer in the bulk rock or handpicked for a separate.

In a magnetic fraction separated from Nakhla, Vieira et al. (1986) found magnetite, ilmenite, and ulvöspinel in small (unspecified) amounts. The Mössbauer spectrum from the paramagnetic fraction of Nakhla showed the presence of a small amount of Fe³⁺; the amount was not specified by Vieira

et al. (1986), but the percentage of Fe³⁺ in pyroxene was later estimated to be 2% (Vistisen et al. 1990).

Note that the oxides and opaque phases reported in these studies are vulnerable to misclassification because they were identified on the basis of optical microscopy and point

counting. For example, in the CV meteorite class, studies using both Mössbauer and XRD to constrain phase proportions have found much less magnetite in Allende than predicted by early petrographic studies and much more than predicted in Vigarano (Phil Bland 2003, personal communication). The discrepancies between petrographic observations and Mössbauer studies noted above may well be the result of the petrography (misclassification of small opaque phases) rather than sample heterogeneity.

In short, the previous work on Mössbauer spectroscopy (MS) of SNC meteorites was limited to understanding how much Fe³⁺ was present and determining its origin to be the result of crystallization conditions, low temperature alteration on the martian surface, shock, or post-terrestrial alteration. With the exception of the few papers by Morris (1997, 1998), no one has attempted to relate the petrography and mineral mode of each meteorite to its whole rock Mössbauer spectrum (as will be needed to understand remotely-acquired Mössbauer data), and the Fe³⁺ measured by Mössbauer spectroscopy has not been related to any particular *f*O₂.

METHODS

In the current study, roughly 200 mg samples of each of 10 SNC meteorites (Table 2) were obtained from JSC, NMNH, and the Vatican. A 10–20 mg chip of each sample was set aside for Mössbauer spectroscopy of the whole rock, and the remaining mass was crushed by hand under acetone to prevent oxidation during grinding. Except in the case of sample EET A79001,B, which was supplied to us as a fine-grained powder unsuitable for separating, phases constituting more than roughly 10% of the mineral mode were hand-picked using a binocular microscope. Note that this method uses only morphology and color as discriminators, so, in some cases, the separates were contaminated by other, similarly colored phases.

The data in italics in Table 2 indicate phases for which separates were prepared by hand picking under a binocular microscope. All separates were first sent to the Keck/NASA Reflectance Experiment Laboratory (RELAB) at Brown University for FTIR, reflectance, and emission spectra before Mössbauer mounts were prepared; those results will be reported elsewhere.

Mössbauer spectra were acquired on mounts prepared by mixing sample powders with sugar under acetone before mounting in a sample holder confined by cello tape. Studies of biotite indicate that this method avoids preferred orientation (Dyar and Burns 1986). For whole rock samples, 20 mg of sample were used; for the mineral separates, sample masses ranged from 1.5–34 mg. The resultant sample thicknesses were well under 1.0 mg Fe/cm², below the thin absorber thickness approximation of Long et al. (1983), so correcting our results for sample thickness was not necessary.

Room temperature Mössbauer spectra were acquired to determine Fe²⁺ and Fe³⁺ contents in the Mineral Spectroscopy Laboratory at Mount Holyoke College. A source of 10–20 mCi ⁵⁷Co in Rh was used on a WEB Research Co. model W100 spectrometer. Run times ranged from 1–10 days. Results were calibrated against an α -Fe foil of 6 μ m thickness and 99% purity.

Spectra were fit using the WMOSS software of WEB Research Co., an implementation of the Voigt-based fitting method for quadrupole splitting distributions (QSD) developed by Rancourt and Ping (1991). Although the WMOSS software package allows use of multiple models for line shape (and Lorentzian and Voigt line shapes were employed to make a point about the ALH A77005 olivine), quadrupole splitting distributions were used to fit all spectra. Because the use of QSDs may be unfamiliar to some readers, a brief overview seems appropriate here.

First, note that this discussion applies only specifically to the transmission mode experiments described in this paper. In this study, the goal is to assess the potential of Mössbauer spectroscopy for discriminating between and quantifying relative amounts of coexisting mineral phases in possible martian rocks, as represented by SNC meteorites. Transmission mode experiments were used because they provide the optimum data for this purpose. In other words, I seek here to understand the fundamental capabilities of this technique under the best of conditions; the capabilities of spectra acquired under other conditions will have similar constraints. In essence, I seek to understand the fundamental abilities of the Mössbauer technique (for example, which commonly occurring, rock-forming minerals have similar Mössbauer parameters?) that are not changed by the method of acquisition. The backscattering geometry used in remote Mössbauer spectroscopy has a similar set of constraints to those for transmission mode experiments, though without the concern for thin absorber corrections. Further information on backscattered Mössbauer spectroscopy is available online in descriptions of the MER and Beagle 2 rovers, as well as in numerous excellent publications by Klingelhöfer (1999) and colleagues (Klingelhöfer et al. 1992, 1996, 1998, and 2000).

The Mössbauer spectrum observed when a transmission experiment is done (as during typical mineralogical experiments) depends on a number of factors, including recoil-free emission and absorption of gamma rays, non-resonant absorption through the Compton and photoelectron effects, and self-absorption in the source. The signal that arrives at the detector in a Mössbauer apparatus is called the transmission integral and represents the signal as a function of the relative velocity between the source and absorber. If a thin-absorber approximation is made (Margulies and Ehrman 1961), the transmission integral becomes a simple sum of pure Lorentzian peaks. When the conditions for the thin-absorber approximation do not apply, as is often the case in mineralogical studies, the line shapes are not Lorentzian, and

a compromise must be made in the model by which the spectrum is treated.

The best way to fit that signal (i.e., the spectrum it generates) continues to be a matter of debate because, as yet, no analytical solution exists for the transmission integral (Vanderberghé et al. 1994). Therefore, various methods for simplifying the problem of fitting the spectra exist; to be thoroughly equipped for mineralogical studies, a lab must be able to use any and all of the existing methods. These include fitting: 1) pure Lorentzian line shapes; 2) a Gaussian distribution of Lorentzian line shapes, known as a Voigt line shape (Voigt 1912); and 3) quadrupole splitting or hyperfine field distributions (Ping et al. 1991; Rancourt and Ping 1991). Only the first of these procedures is commonly in use worldwide, largely because commercial software for the latter methods has only recently become available.

However, the approach of fitting quadrupole splitting distributions (QSD) has been shown to be superior to the Lorentzian-based approach in spectra in which there are poorly resolved quadrupole pairs, as is certainly the case in olivine, pyroxene, and whole rock spectra. It works best in samples where the Fe atoms are not surrounded by a perfectly homogeneous array of neighbors and next nearest neighbor. Effectively, the QSDs model the local distortions and atomic disorder surrounding the Fe atoms rather than simply reflecting the ideal point symmetries of the relevant sites (Rancourt 1994a). In a series of papers (Rancourt 1994a, b; Rancourt et al. 1994), Rancourt and coworkers convincingly demonstrated that the QSD method performs better than Lorentzian fits in a number of ways. Fits with Lorentzian doublets tend to overestimate the spectral backgrounds, put large wings or tails on the main absorption peaks, and give unphysically large linewidths (Rancourt 1994a). As noted by Rancourt (1994b), “fitting with Lorentzian doublets can at best give phenomenological characterizations of spectra, while QSDs are true physical quantities amenable to theoretical calculations and crystal chemical interpretation.” Because one of the goals of the current study is to use Mössbauer spectra of SNCs to extract information about sites and valences in different minerals, QSD fits are used to model the spectra here.

In all the fits presented here, following the established conventions for fits using quadrupole splitting distributions, γ , which is the Lorentzian full peak width and half maximum intensity, was constrained to be 0.20 mm/s, which is roughly the natural linewidth of Fe. Use of the QSD model obviates the need to allow line width to vary explicitly. The ratio of Lorentzian heights of the 2 lines in an elemental quadrupole doublet, h_+/h_- , was constrained for all components to be equal to one. All the other parameters, including the center of a Gaussian component of the Δ distribution (Δ_0), the width of the quadrupole splitting distribution (δ_Δ), the value of isomer shift (δ) when the distributed hyperfine parameter has a value of zero (δ_0), the coupling of δ to the distributed hyperfine

parameter (δ_1), and the relative area of the doublets (A) were allowed to vary freely. Isomer shift (δ) is calculated using $\delta = \delta_1 \times \Delta_0 + \delta_0$. Details relating to the application of these parameters can be found in Rancourt and Ping (1991).

Errors vary according to the quality of the spectra (which reflect the total Fe contents and amount of sample measured) but are usually estimated to be ± 0.3 –3% absolute, so most Fe^{3+} contents in these samples are right at our detection limits; this was also the case for previous studies. Values of χ^2 are given in tables of fit parameters. But, note that these cannot be compared between fits of different spectra as discussed in Ruby (1973). The “worst” value of χ^2 , for example, is the fit to the best spectrum obtained here; this occurs because the data are of such high quality that they are difficult to fit. χ^2 values are primarily of use in distinguishing different fits to the same spectrum. For example, in a noisy spectrum, the error bars are quite large, so a large number of satisfactory fits will pass through the data points within those large errors bars. If the spectra are of very high quality, a much smaller number of possible fits will pass through the smaller error bars.

RESULTS

Olivine Spectra

Olivine spectra are shown in Fig. 1, and Mössbauer parameters of their fits are given in Table 3. Of these, the simplest is that of Chassigny, with 2 doublets representing Fe^{2+} . The largest doublet (89.8% of the total area) is Fe^{2+} in octahedral coordination in olivine. The parameters of smaller doublets ($\delta = 1.15$, $\Delta_0 = 2.54$, $\delta_\Delta = 1.806$ mm/s) suggest either the presence of a small amount of Fe^{2+} in an impurity or the presence of a second distribution also arising from olivine, but a doublet with those parameters (especially such low quadrupole splitting) has not yet been reported in the literature. To test this possibility, a Mössbauer spectrum of a San Carlos olivine-analogue synthetic olivine (kindly lent by Steve Mackwell) was run and fit with the QSD model. Although this sample is undeniably pure olivine (albeit with a different bulk composition), it also contains a second broad distribution with octahedral parameters and low quadrupole splitting for Fe^{2+} at $\delta = 1.10$ mm/s, $\Delta_0 = 2.33$ mm/s, and $\delta_\Delta = 2.334$ mm/s. Thus, use of the QSD model makes apparent the presence of a second, minor distribution in olivine spectra. The reflectance IR spectra of the Chassigny mineral separate also showed only olivine features (unpublished work). We conclude that the Chassigny spectrum represents that of pure olivine.

The spectrum of ALH A77005 olivine is shown fitted in several ways in Fig. 1, using models employing Lorentzian, Voigt, and QSD lineshapes. Based on differences in χ^2 , the QSD models clearly fit the data the best. At issue is the fact that both the 100% Fe^{2+} and the 99.5% Fe^{2+} QSD models have comparable χ^2 . Under unconstrained circumstances, the

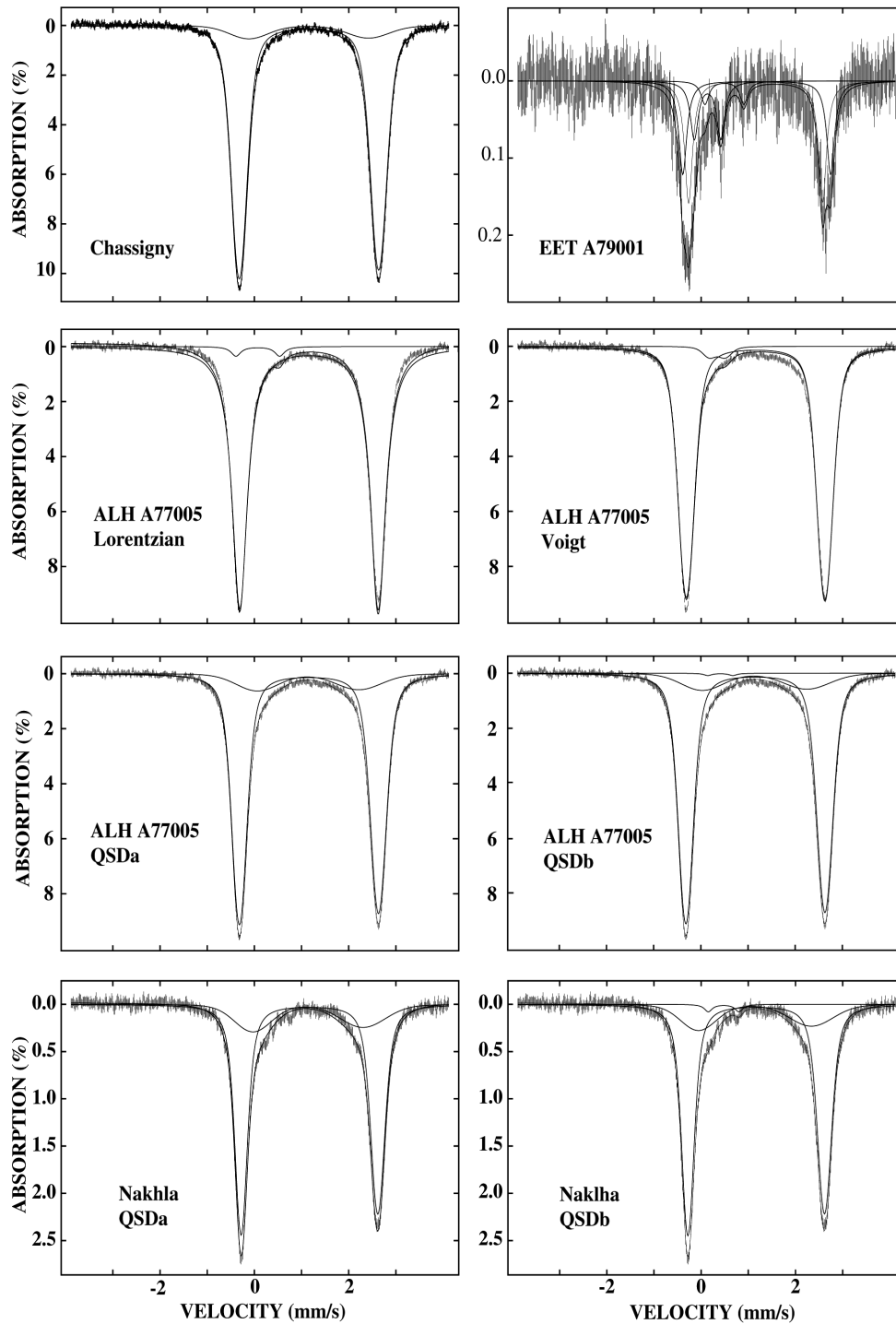


Fig. 1. Mössbauer spectra of olivine separates from SNC meteorites.

pure Fe^{2+} model would be preferred on the basis of its simplicity. However, the previously cited work by Ostertag et al. (1984) shows EPR and optical spectra that confirm (but do not quantify) the presence of Fe^{3+} in small amounts, so the QSD model with a small Fe^{3+} contribution is probably the best interpretation of these data. Ostertag et al.'s Mössbauer spectrum was fit (using a Lorentzian lineshape) with 1 Fe^{3+}

doublet that constituted 4.5% of the total peak area, and this is comparable to the areas of the Lorentzian (2.3% Fe^{3+}) and Voigt (3.4% Fe^{3+}) fits here. So, the value reported by Ostertag et al. (1984) may be slightly high due to the line shape used (note that the QSD model was not proposed until several years after Ostertag's work). Apparently, the use of the QSD model may give a more realistic value for the amount of Fe^{3+}

Table 3. Mössbauer parameters for olivine separates from SNC meteorites.^a

	Chassigny QSD	ALH A77005 Lor.	ALH A77005 Voigt	ALH A77005 QSDa	ALH A77005 QSDb	Nakhla QSDa	Nakhla QSDb	EET A79001 QSD
Fe²⁺ (cpx?)								
Δ_0	2.54	–	–	2.15	2.22	2.34	2.40	–
δ_Δ	1.81	–	–	2.00	2.00	1.85	1.79	–
δ_0	1.11	–	–	1.09	1.09	1.01	1.01	–
δ_1	0.02	–	–	0.02	0.03	0.05	0.06	–
δ	1.15	–	–	1.14	1.14	1.14	1.14	–
Δ	–	–	–	–	–	–	–	–
A	10.2%	–	–	14.1%	14.1%	22.8%	20.9%	–
Fe²⁺ (ol)								
Δ_0	2.96	–	–	2.95	2.95	2.90	2.90	3.13
δ_Δ	0.59	–	–	0.55	0.55	0.43	0.43	0.00
δ_0	1.11	–	–	1.09	1.09	1.01	1.01	1.30
δ_1	0.02	–	–	0.02	0.03	0.05	0.06	–0.04
δ	1.16	1.16	1.16	1.12	1.16	1.17	1.17	1.18
Δ	–	2.93	2.94	–	–	–	–	–
A	89.8%	97.7%	96.6%	85.9%	85.4%	77.2%	77.3%	31.5%
Fe²⁺ (ol)								
Δ_0	–	–	–	–	–	–	–	2.84
δ_Δ	–	–	–	–	–	–	–	0.00
δ_0	–	–	–	–	–	–	–	1.18
δ_1	–	–	–	–	–	–	–	–0.07
δ	–	–	–	–	–	–	–	1.15
A	–	–	–	–	–	–	–	41.1%
Fe³⁺ (ol)								
Δ_0	–	–	–	–	0.53	–	0.65	0.82
δ_Δ	–	–	–	–	0.00	–	0.00	0.00
δ_0	–	–	–	–	0.80	–	0.41	0.23
δ_1	–	–	–	–	–0.73	–	0.10	0.32
δ	–	0.07	0.34	–	0.41	–	0.48	0.49
Δ	–	0.93	0.34	–	–	–	–	–
A	–	2.3%	3.4%	–	0.5%	–	1.8%	7.9%
Fe³⁺ (ox?)								
Δ_0	–	–	–	–	–	–	–	0.56
δ_Δ	–	–	–	–	–	–	–	0.00
δ_0	–	–	–	–	–	–	–	0.14
δ_1	–	–	–	–	–	–	–	–0.01
δ	–	–	–	–	–	–	–	0.13
Δ	–	–	–	–	–	–	–	–
A	–	–	–	–	–	–	–	19.4%
χ^2	0.66	2.99	2.77	0.64	0.63	0.48	0.42	0.41

^aResults are given in mm/s relative to the center point of a Fe foil calibration spectrum. QSD refers to fits using the quadrupole splitting distribution model; Lor. and Voigt fits use Lorentzian and Voigt line shapes, respectively. Use of the letter (a) or (b) indicates multiple fits using the same line shape. The Lorentzian full peak width and half maximum intensity (γ) was constrained to be 0.20 mm/s, which is the natural linewidth of Fe. Δ_0 = the center of a Gaussian component of the Δ distribution. δ_Δ = the width of the quadrupole splitting distribution. δ_0 = the value of isomer shift (δ) when the distributed hyperfine parameter has a value of zero. δ_1 = the coupling of δ to the distributed hyperfine parameter. $\delta = \delta_1 \times \Delta_0 + \delta_0$. A = the relative area of the doublet. h_+/h_- = the ratio of Lorentzian heights of the 2 lines in an elemental quadrupole doublet, which was constrained for all components to be equal to one. Details can be found in Rancourt and Ping (1991).

in this sample, which is roughly 0.5% of the total Fe. This is, then, consistent with the 4.2 K spectrum acquired by Burns (1989), who estimated the amount of Fe³⁺ in ALH A77005 to be <2% of the meteorite.

The Mössbauer spectrum of Nakhla is also shown in Fig. 1, with parameters given in Table 3, and, once again, Fe³⁺ is right at the detection limit of the technique. Lacking other

types of spectroscopy to corroborate its presence, the Fe³⁺ contents can only be noted to be in the range of 0–1.8%.

The Mössbauer spectrum of the olivine separate from EET A79001,A is noisy (Fig. 1) because only a very small amount of olivine was present modally (8.9%; McSween and Jarosewich 1983), and the spectrum was acquired on only 4.5 mg of separate. However, this spectrum is significantly

different from those of the other SNC olivines (Table 3). A total of 4 doublets was required to produce a fit through all the data points in this spectrum, largely because this sample has more Fe³⁺ than any of the other olivines studied. No evidence exists of any contamination from pyroxene, but 2 Fe²⁺ doublets with parameters like those of previously published olivine spectra are found (Dyar et al. 1989). A doublet with parameters resembling those previously reported for Fe³⁺ in olivine is also present (McGuire et al. 1991), constituting 7.9% of the total area. A distribution with parameters corresponding to tetrahedral Fe³⁺ is also present; this is unlikely to correspond to either the ilmenite or the ulvöspinel reported by Steele and Smith (1982). It probably represents a nanophase oxide in very minute amounts.

The most interesting question arising from the spectrum of the “olivine” separate from EET A79001,A is the origin of its Fe³⁺. Work by McCanta and Rutherford (2002) suggests that the fO_2 of this sample is roughly IW + 2.4, making it the second most oxidized sample studied by Eu oxybarometry. This is consistent with the presence of the observed 7.9% Fe³⁺. Alternatively, this separate could represent olivine xenocrysts that have been reported in this meteorite (McSween and Jarosewich 1983; Middlefehldt et al. 1997) and that, therefore, would not represent the magmatic oxidation state of the bulk sample.

Pyroxene Spectra

Mössbauer spectra of pyroxene separates from 7 SNC meteorites are shown in Fig. 2; fit parameters are given in Table 4. The most frustrating thing about this data set is that all the samples studied, with the exception of Nakhla and ALH 84001, contain either mixtures of clino- and orthopyroxene and/or both high-Ca and low-Ca clinopyroxene, sometimes in 2 distinct populations and sometimes in a continuous range of compositions. This variation is important because the bulk chemistry of the pyroxene controls its crystal structure, and, thus, steric constraints may place limits on the incorporation of Fe³⁺ into pyroxene as a function of composition. Orthopyroxene and low-Ca clinopyroxene rarely incorporate greater than 15% of the total Fe as Fe³⁺ in terrestrial occurrences, while higher Ca cpx can contain up to 50–60% Fe³⁺ (Deer et al. 1978). So, the Mössbauer spectra in this study likely represent unresolvable mixtures of low-Fe³⁺, low- or no-Ca pyroxene with potentially high-Fe³⁺, high-Ca pyroxene. Because the sites in the different types of pyroxene are so similar, cpx and opx cannot be quantitatively distinguished by Mössbauer spectroscopy, and, thus, any Fe³⁺ observed in the spectra may not be assigned to its proper host.

This mixture of overlapping clino- and orthopyroxene distributions is evident in Table 4. Four different distributions of Fe²⁺ in octahedral coordination are resolved. Note that the ALH 84001 has a distribution with $\delta = 1.16$ mm/s and $\Delta = 2.22$ mm/s that is characteristic of opx. It is also the only

pyroxene studied to have no Fe³⁺. All the other clinopyroxene and ortho-clinopyroxene mixtures contain a small amount of Fe³⁺ in basically indistinguishable quantities ranging from 1.4–2.3% of the total Fe. Our spectra are similar to the Nakhla pyroxene spectrum published by Vieira et al. (1986).

Whole Rock Spectra

Room temperature whole rock Mössbauer spectra of the 11 samples studied are shown in Fig. 3, and Mössbauer parameters of their fits are given in Table 5. The whole rock spectra are an amalgamation of the Fe atoms in all minerals present. A common misconception about Mössbauer spectra of mineral mixtures is that the areas of doublets (referred to as “distributions” if the QSD model is used) are proportional to the modal abundance of the minerals they represent. This is very rarely true, and it occurs only if 2 conditions are satisfied: 1) the proportion of Fe atoms to all the other atoms in the structure is the same in each phase in the rock; and 2) the molar volumes of the phases are the same. For mixtures of olivine, pyroxene, and oxide, these conditions are explicitly not satisfied, and, therefore, the fact that areas given in Table 5 do not correspond in any way to mineral modes must be stressed. If the compositions of the individual phases are known such that mineral formulas can be calculated, only then is it possible to extract modal information from the spectra (see the Discussion section, below).

Given this background, comparing the whole rock spectra to those of the minerals separated from them is interesting. In some cases, such as ALH A77005, the whole rock spectrum is basically indistinguishable from the mineral separate (in that case, olivine) because the phases other than the one separated are not Fe-rich or our starting chip of that meteorite happened to be mostly monomineralic.

ALH 84001 is also nearly monomineralic, and its whole rock spectrum closely resembles that of the opx separated from it. However, the smaller distributions in the spectrum show contributions from at least 2 other types of Fe, probably in multivalent chromite, 2.6% (Fe²⁺) and 4.5% (Fe³⁺) of the total Fe. Although the chromite only constitutes 2% of the mineral mode, its Fe content is significantly higher than that of the coexisting opx, so its contribution to the Mössbauer spectrum is significant.

The whole rock spectrum of Chassigny has 91.6% of the total Fe as Fe²⁺ in olivine, but the remaining 8.4% of the Fe is in a mixture of Fe²⁺ sites that gives rise to parameters of $\delta = 1.074$ and $\Delta_0 = 2.193$ mm/s; this distribution probably results from a mixture of oxide and melt.

The whole rock spectrum of Zagami is nearly identical to that of its pyroxene separate, with no sign of potential contamination from oxide or sulfate. For LEW 88516, EET A79001,A, and Nakhla, whole rock Mössbauer spectra combine both olivine and pyroxene, one would estimate the amount of Fe²⁺ in each mineral if the recoil-free fractions for

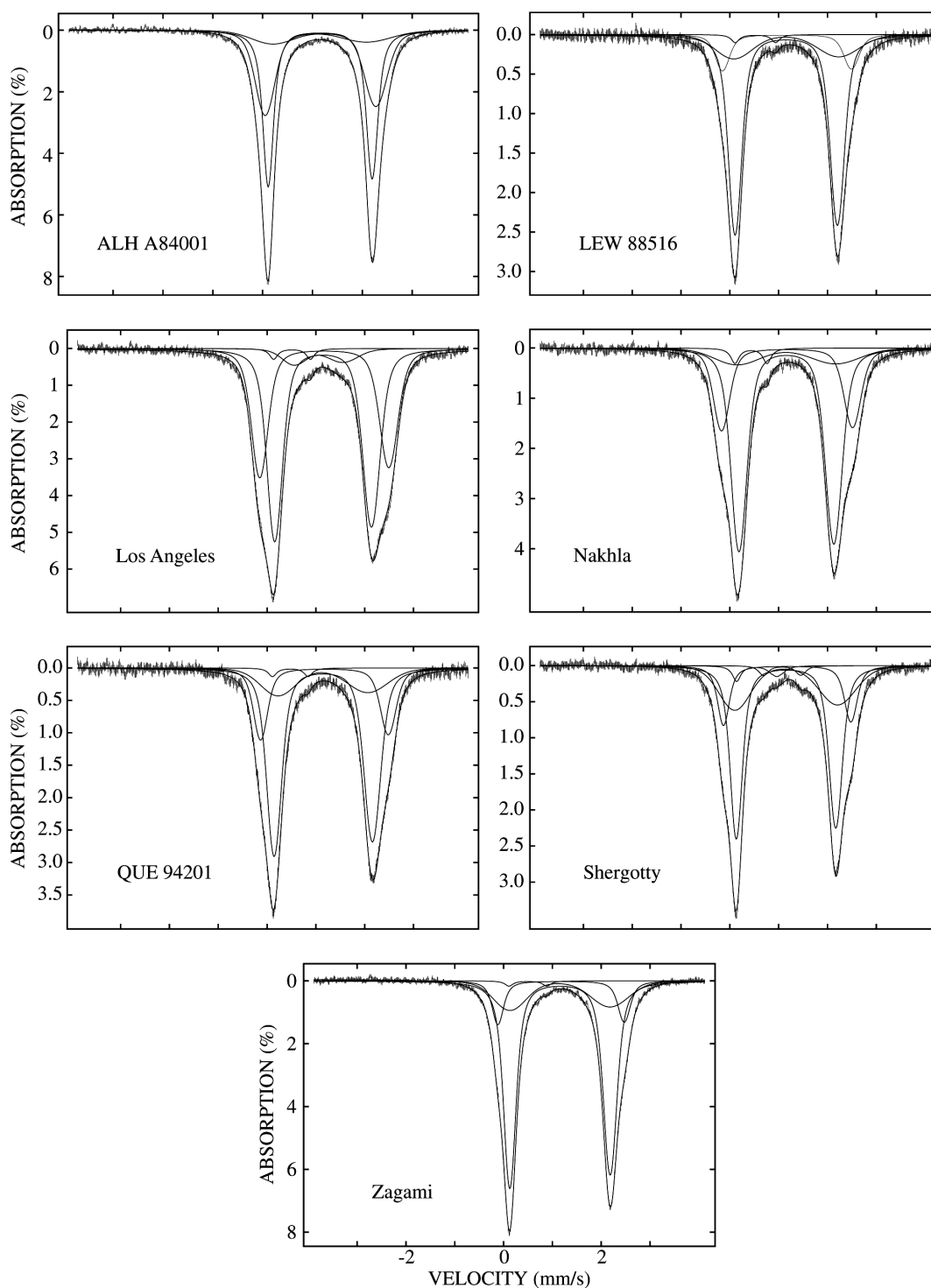


Fig. 2. Mössbauer spectra of pyroxene separates from SNC meteorites.

both minerals were known (but, see below!). A small amount of Fe^{3+} is also found in both spectra, but telling which mineral(s) the Fe^{3+} occupies is impossible.

The whole rock spectrum of QUE 94201 resembles that of its cpx separate with the addition of ilmenite peaks that are prominent around 0.4 and 1.4 mm/s. The spectrum of EET

A79001,B also has ilmenite peaks, along with 2 distributions assigned to pyroxene and a small Fe^{3+} peak (consistent with the wet chemical analysis reported by McSween 1983). The Shergotty whole rock spectrum also contains Fe^{2+} in pyroxene, a small amount of oxide, and a Fe^{3+} distribution that cannot be assigned to a specific mineral.

Table 4. Mössbauer results for pyroxene in SNC meteorites.^a

	ALH 84001	LEW 88516	Los Angeles	Nakhla	QUE 94201	Shergotty	Zagami
Fe ²⁺ (px)							
Δ_0	–	2.64	2.64	2.68	2.62	2.63	2.59
δ_Δ	–	0.48	0.62	0.58	0.49	0.32	0.32
δ_0	–	1.10	1.08	1.12	1.07	1.08	1.07
δ_1	–	0.03	0.04	0.02	0.04	0.04	0.04
δ	–	1.17	1.17	1.17	1.18	1.18	1.18
A	–	12.8%	37.8%	24.8%	21.6%	11.6%	12.9%
Fe ²⁺ (px)							
Δ_0	2.22	2.14	–	–	–	–	–
δ_Δ	0.77	1.69	–	–	–	–	–
δ_0	1.06	1.10	–	–	–	–	–
δ_1	0.05	0.03	–	–	–	–	–
δ	1.16	1.16	–	–	–	–	–
A	40.5%	18.5%	–	–	–	–	–
Fe ²⁺ (px)							
Δ_0	2.09	2.10	–	2.02	2.01	2.09	2.05
δ_Δ	0.26	0.43	–	2.08	0.53	1.24	1.50
δ_0	1.06	1.10	–	1.12	1.07	1.08	1.07
δ_1	0.05	0.03	–	0.02	0.04	0.04	0.04
δ	1.16	1.16	–	1.16	1.15	1.16	1.16
A	46.7%	66.9%	–	12.1%	58.9%	27.3%	20.6%
Fe ²⁺ (px)							
Δ_0	1.88	–	1.98	1.94	1.84	2.05	2.06
δ_Δ	2.00	–	0.57	0.57	1.62	0.47	0.39
δ_0	1.06	–	1.08	1.12	1.07	1.08	1.07
δ_1	0.05	–	0.04	0.02	0.04	0.04	0.04
δ	1.15	–	1.15	1.16	1.15	1.16	1.16
A	12.8%	–	53.8%	60.3%	17.7%	59.4	72.8%
Fe ²⁺ (ox)							
Δ_0	–	–	1.00	–	–	–	–
δ_Δ	–	–	1.09	–	–	–	–
δ_0	–	–	0.99	–	–	–	–
δ_1	–	–	0.06	–	–	–	–
δ	–	–	1.06	–	–	–	–
A	–	–	6.5%	–	–	–	–
Fe ³⁺ (px)							
Δ_0	–	0.82	0.75	0.66	0.73	0.79	0.77
δ_Δ	–	0.00	0.05	0.05	0.00	0.00	0.05
δ_0	–	0.53	0.39	0.13	0.46	0.44	0.50
δ_1	–	–0.01	0.16	0.46	0.02	0.02	–0.04
δ	–	0.52	0.51	0.43	0.48	0.46	0.50
A	–	1.8%	1.9%	2.3%	1.7%	1.7%	1.4%
χ^2	0.79	0.45	0.91	0.53	0.49	0.42	0.59

^aResults are given in mm/s relative to the center point of a Fe foil calibration spectrum. The symbols and constraints are as in Table 3.

The spectrum of the whole rock Los Angeles meteorite is very complex. No contribution from olivine is evident, but a small distribution with $\delta = 1.12$ mm/s and $\Delta = 1.402$ mm/s is 6.6% of the spectral area. This peak may well be from sulfide. Doublets assigned to pyroxene, ilmenite, and Fe³⁺ are also present in at least one of the phases. Unfortunately, even in this high quality spectrum acquired under the best of terrestrial lab conditions, identifying specific phases on the basis of the Mössbauer spectrum is impossible. This spectrum is a good example of the type of undecipherable data that might be obtained remotely on the martian surface, only with

possibly less resolution (some MER spectra will be acquired over a velocity range of ± 10 mm/s instead of ± 4 mm/s as is done here) and in backscatter mode. Without the independent knowledge of what phases are present in this sample, identifying anything in this spectrum, with the possible exception of ilmenite, would be impossible. The other distributions have parameters that would allow them to be assigned to virtually any silicate in which octahedral sites exist, and moreover, assigning the Fe³⁺ to any particular phase would be impossible. This problem occurs because site geometries and neighbors are similar for Fe atoms in silicates,

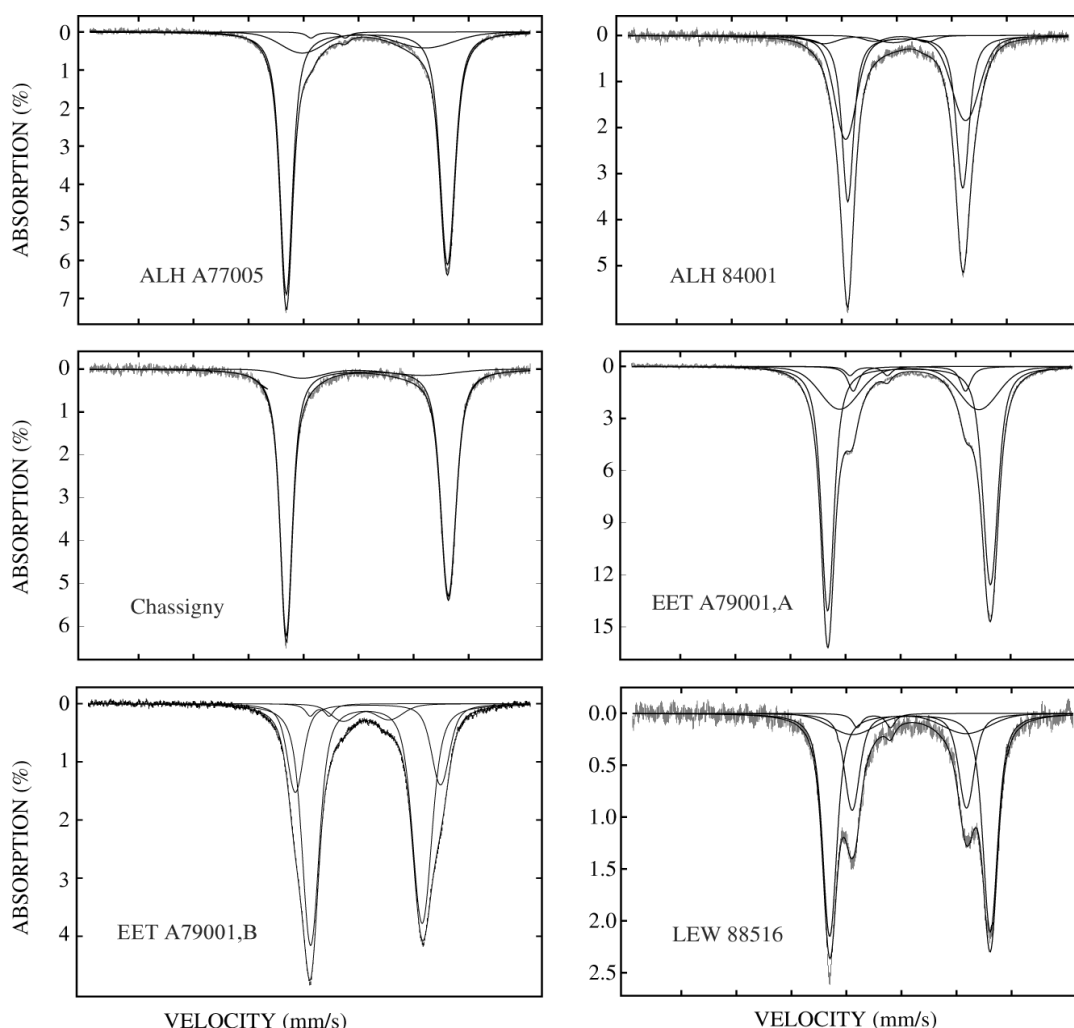


Fig. 3. Mössbauer spectra of bulk rock samples of SNC meteorites.

and, therefore, Mössbauer parameters of many silicates are fundamentally similar.

Because one of the stated goals of this work is to relate SNC meteorite Mössbauer spectra to those acquired remotely on the martian surface, the reason that only room temperature spectra are used in this paper must be explained. Martian surface temperatures cover a range from roughly 140–280 K, and the landing site temperature variations for the MER and Beagle 2 landers are not yet well-known. Thus, predicting an appropriate “Mars-analogous” temperature at which to acquire whole rock temperatures would have been difficult. Our group is currently acquiring Mössbauer spectra of the mineral separates described in this study at small increments over this range of possible Mars surface temperatures. As is also known from the literature (e.g., DeGrave and van Alboom 1991), the Mössbauer spectra of all the minerals we are studying here change dramatically over this range. These changes, which define a Mössbauer temperature and a recoil-free fraction for each Fe site and valence state in each individual phase, are too complex to be described here. Interested readers are directed

to the Mars Mineral Spectroscopy Database Web site at <http://www.mtholyoke.edu/go/mars> for inspection of variable temperature Mössbauer spectra of the various phases involved.

DISCUSSION

Significance of Brown Olivine

The revised estimate of the Fe^{3+} content of ALH A77005 brown olivine, as suggested above, again raises the interesting issue of the significance of brown olivine. Clearly, from the work of Ostertag et al. (1984), the cause of the brown color is the presence of a small amount of octahedral Fe^{3+} . However, by analogy with numerous other silicates, the amount of Fe^{3+} could be extremely small (ppm) and still give rise to the brown color. The more interesting question, then, is where does the Fe^{3+} come from? Ostertag et al. (1984) suggested either oxidation of the sample on the martian surface or oxidation caused by shock-induced impact. The latter

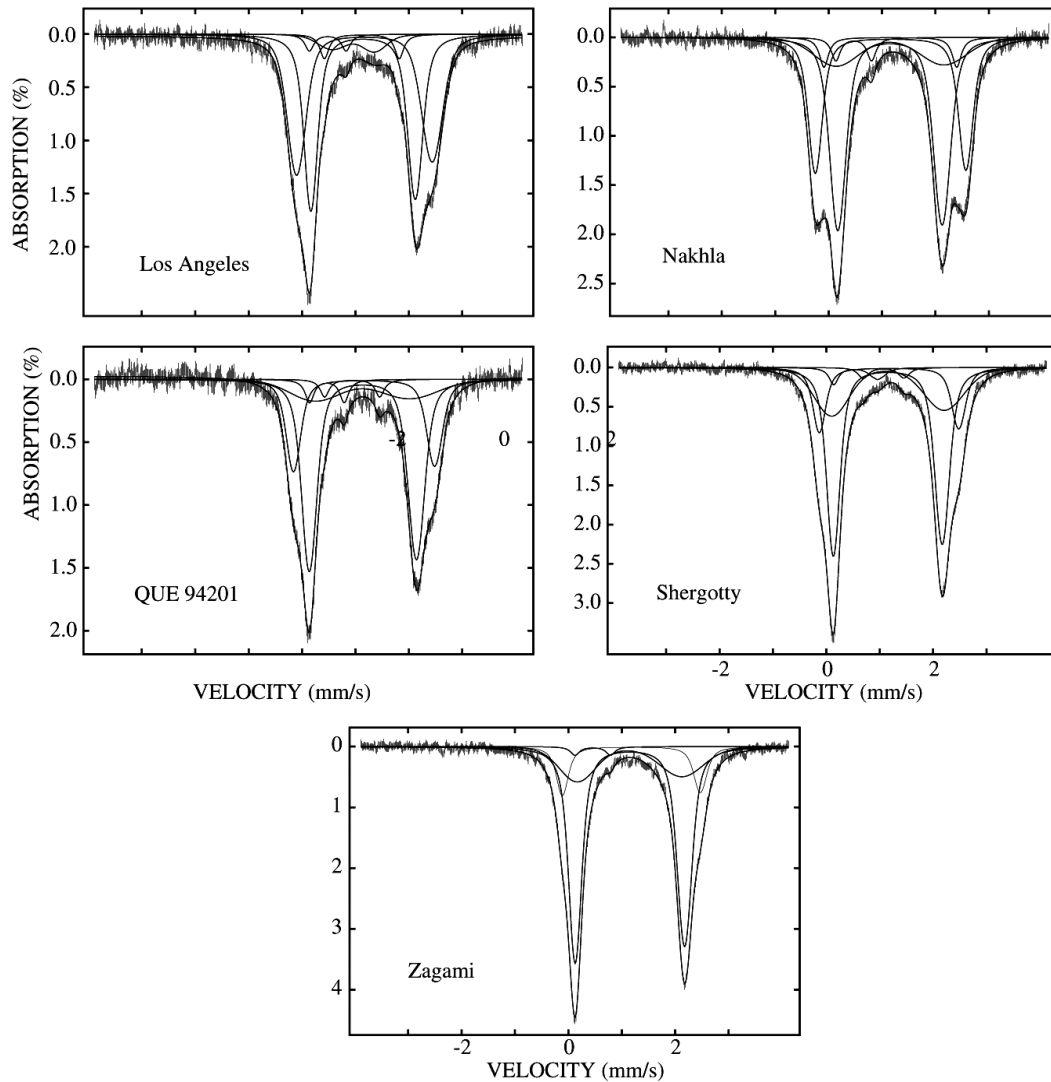


Fig. 3. Mössbauer spectra of bulk rock samples of SNC meteorites. *Continued.*

suggestion was backed up by the work of Bauer (1979), suggesting that brown olivine = shocked olivine. This is also consistent with the presence of brown olivine in LEW 88516, the other SNC meteorite believed to have been heavily shocked.

However, an alternative hypothesis exists to explain the brown color. In work on recently erupted mantle xenoliths from the Cima volcanic fields in the southern Mojave desert, this author has also observed brown olivine, though it is obviously unshocked. Mössbauer spectra of olivine separates from these localities show no Fe^{3+} detectable by Mössbauer (i.e., probably <1%), but they are nonetheless unmistakably brown. Thus, the presence of brown color in olivine does not necessarily imply a history of shock. However, the Mojave brown olivines do have one thing in common with the SNC meteorites: both may have come from source regions that started out to be hydrous, such that the original magmatic olivines may have incorporated a considerable amount of H

into their structures (cf., the work of George Rossman and his students on H contents in anhydrous mantle olivines: Bell and Rossman 1992; Miller et al. 1987; Rossman 1990). Either ascent or shock processes could dehydrogenate the olivine via the mechanism $\text{H}^+_{\text{mineral}} + \text{Fe}^{2+}_{\text{mineral}} = \frac{1}{2}(\text{H}_2)_{\text{gas}} + \text{Fe}^{3+}_{\text{mineral}}$. The diffusivity of H is fast enough for partial dehydrogenation to occur during ascent from the Earth's mantle (Kohlstedt and Mackwell 1998; Mackwell and Kohlstedt 1990) and is certainly fast enough to occur during a high temperature and pressure shock event. The solubility of hydrogen in olivine at terrestrial mantle conditions is 0.03 wt% H_2O (Bai and Kohlstedt 1992, 1993); this number may seem small, but that is because it is expressed as wt%. Consider the average composition of the olivine in ALH A77005 given by McSween et al. (1979). If the olivine once contained 0.03 wt% H_2O , that would constitute about 0.005 atoms pfu H. If all the excess charge from H was transferred to the roughly 0.56 atoms pfu of Fe^{2+} during shock or transport, the resultant 0.005 atoms pfu

Table 5. Mössbauer results for bulk rock SNC meteorites.^a

	ALH A77005	ALH A84001	Chassigny	EET A79001,A	LEW 88516	Los Angeles	Nakhla	QUE 94201	Shergotty	Zagami
Fe²⁺ Ol										
Δ_0	2.93	–	2.95	2.96	2.92	–	2.82	–	–	–
δ_Δ	0.34	–	0.34	0.34	0.37	–	0.38	–	–	–
δ_0	0.91	–	0.83	0.93	1.12	–	1.12	–	–	–
δ_1	0.08	–	0.11	0.08	0.01	–	0.01	–	–	–
δ	1.15	–	1.16	1.15	1.16	–	1.16	–	–	–
A	80.8%	–	91.6%	64.3%	57.1%	–	29.1%	–	–	–
Fe²⁺										
Δ_0	–	–	–	2.53	–	2.54	2.49	2.64	2.61	2.58
δ_Δ	–	–	–	1.46	–	0.66	0.04	0.43	0.34	0.29
δ_0	–	–	–	1.17	–	1.06	1.12	1.07	1.07	1.05
δ_1	–	–	–	–0.00	–	0.04	0.01	0.03	0.04	0.06
δ	–	–	–	1.16	–	1.17	1.16	1.16	1.18	1.18
A	–	–	–	28.1%	–	43.3%	4.7%	24.1%	16.6%	13.0%
Fe²⁺										
Δ_0	2.24	2.18	2.19	2.04	2.08	1.96	2.02	2.01	2.11	1.96
δ_Δ	1.20	0.85	2.00	0.16	0.41	0.39	1.80	0.47	1.44	1.55
δ_0	0.91	1.00	0.83	1.17	1.12	1.06	1.12	1.07	1.07	1.05
δ_1	0.08	0.08	0.11	–0.00	0.01	0.04	0.01	0.03	0.04	0.06
δ	1.09	1.16	1.07	1.16	1.14	1.14	1.15	1.14	1.15	1.15
A	17.5%	47.1%	8.4%	5.7%	26.0%	42.7%	16.1%	52.0%	27.8%	23.1%
Fe²⁺										
Δ_0	–	2.09	–	–	2.07	1.40	1.95	1.77	–	2.05
δ_Δ	–	0.25	–	–	1.76	0.00	0.50	2.19	–	0.37
δ_0	–	1.00	–	–	1.12	1.06	1.12	1.07	–	1.05
δ_1	–	0.08	–	–	0.01	0.04	0.01	0.03	–	0.06
δ	–	1.16	–	–	1.14	1.12	1.15	1.13	–	1.15
A	–	45.8%	–	–	14.2%	4.4%	46.5%	16.3%	–	62.0%
Oxide										
Δ_0	–	0.95	–	–	–	0.79	–	1.03	0.76	–
δ_Δ	–	0.62	–	–	–	0.96	–	0.02	0.20	–
δ_0	–	1.12	–	–	–	1.00	–	1.08	1.05	–
δ_1	–	–0.07	–	–	–	–0.05	–	–0.13	0.04	–
δ	–	1.06	–	–	–	0.96	–	0.94	1.07	–
A	–	2.6%	–	–	–	6.6%	–	3.3%	2.4%	–
Fe³⁺										
Δ_0	0.62	1.26	–	0.68	0.61	0.69	0.67	0.65	0.82	0.66
δ_Δ	–0.03	1.04	–	0.00	0.05	0.06	0.00	0.00	0.20	0.00
δ_0	0.80	0.25	–	0.45	0.27	0.40	0.43	0.48	0.03	0.48
δ_1	–0.57	0.05	–	–0.05	0.38	0.12	0.06	–0.03	0.64	–0.03
δ	0.44	0.31	–	0.42	0.50	0.48	0.47	0.47	0.55	0.46
A	1.5%	4.5%	–	1.9%	2.7%	3.0%	3.6%	4.3%	3.4%	1.9%
χ^2	1.66	0.44	0.71	2.34	0.68	0.56	0.68	0.46	0.48	0.51

^aResults are given in mm/s relative to the center point of a Fe foil calibration spectrum. The symbols and constraints are as in Table 3.

Fe³⁺ would be 0.9% of the total Fe. That value is larger than the 0.5% Fe³⁺ measured in this study and is right at the detection limit of Mössbauer spectroscopy. Thus, possibly the brown olivines observed in ALH A77005 (and those in other meteorites as well) are brown because they once contained H. Such an interpretation would explain not only the observed brown olivines in highly shocked natural and experimentally shocked samples but also the brown color of some erupted

terrestrial mantle olivines. Further experimental studies of the effects of shock on “hydrous” and anhydrous olivine single crystals are currently in progress at JSC to test this hypothesis.

Note that if the cause of the brown color in olivine is indeed dehydrogenation, then this implies that the starting compositions of the olivines might be as hydrous as those found on Earth. This is consistent with the presence of hydrous phases such as amphibole in various SNC meteorites

(Dyar et al. 2000) and with geochemical and petrologic evidence for magmatic water within Mars, as reported by Minitti and Rutherford (2000), Danni et al. (2001), and McSween et al. (2001).

Distinguishing Between opx and cpx with Mössbauer

One of the most critical tools of the field of planetary remote sensing is the ability to use the 1 and 2 μm bands to distinguish among various species of pyroxene. Can Mössbauer spectra distinguish between these species? On the basis of more than 100 pyroxene spectra acquired in my Mössbauer lab (e.g., Dyar et al. 1989, 1992, 1996; McGuire et al. 1991), the most obvious difference between opx and cpx is the position of the M2 doublet/distribution, which lies at about $\Delta = 2.17$ mm/s in opx and $\Delta = 2.01$ mm/s in cpx. In the SNC data set, only the ALH 84001 opx has a doublet in this diagnostic opx region ($\Delta = 2.22$ mm/s). The LEW 88516 pyroxene separate, which is a mixture of cpx and opx, has a distribution at $\Delta = 2.14$ mm/s, while all the other pyroxenes, which are very fine scale mixtures of high- and low-Ca clinopyroxene, have the distribution at $\Delta = <2.10$ mm/s. So, to some extent, in high resolution spectra, the energy of the distribution located at $\delta = 1.16$ mm/s and $\Delta = 2.05\text{--}2.25$ mm/s is diagnostic of the type of pyroxene that is present.

So, is distinguishing between opx and cpx possible in a bulk rock spectrum where the pyroxene is mixed with other phases? The answer is: not entirely. Consider the third horizontal set of Fe^{2+} data in Table 5, where the values for Δ_0 for the third Fe^{2+} distribution are tabulated. ALH A77005 has the highest Δ_0 value of 2.24; this sample has 9.5% modal opx and 3.7% modal cpx. ALH 84001 (all opx) and Chassigny (with a compositional range from $\text{Wo}_{33}\text{En}_{49}\text{Fs}_{17}$ to $\text{Wo}_3\text{En}_{68}\text{Fs}_{17}$) have distributions with $\Delta_0 = 2.18$ mm/s and 2.19 mm/s, respectively, indicative of the presence of opx. However, LEW 88516, which has 25.3% modal opx, has a Δ_0 value of 2.079 mm/s. The conclusion here is that while the presence of $\Delta_0 \approx 2.2$ mm/s distributions in the Mössbauer spectra of bulk rocks is a good predictor of the presence of opx, the absence of a distribution at that energy does not rule out the existence of opx.

Distinguishing Between Pyroxene and Olivine

Although discriminating among pyroxene compositions in a whole rock Mössbauer spectrum may be a lost cause, distinguishing between olivine and pyroxene is not so difficult. Given that Fe^{2+} in olivine routinely has (relatively unusual) quadrupole splittings of 2.88–3.10 mm/s (Dyar et al. 1989), the appearance of Fe^{2+} peaks with $\Delta > 2.75$ mm can be considered confirmation of the presence of olivine, at least in the majority of commonly occurring rocks.

However, quantifying the ratio of olivine to another phase is dependent on knowledge of recoil-free fractions (f)

of those phases. This Mössbauer or recoilless fraction is the fraction of nuclear events that take place without exciting the lattice; i.e., they produce no change in the quantum state of the lattice. This fraction of the recoil energy that cannot be transferred to exciting a lattice vibration can be quantified as:

$$f = [\exp(-4\pi^2 \langle X^2 \rangle) \lambda^2]$$

where $\langle X^2 \rangle$ is the mean square vibrational amplitude of the absorbing/transmitting nucleus in the solid, and λ is the wavelength of the γ photon. The value of $\langle X^2 \rangle$ (typically in the range of 10^{-4} \AA^2) varies for different chemical compounds depending on the site geometry and valence state of the Fe atom. Therefore, f also varies for different valence states of iron in different types of sites (and minerals).

The area of a Mössbauer doublet (pair of peaks) is actually a function of peak width (Γ), sample saturation ($G[x]$), and the Mössbauer recoil-free fraction (f) as just discussed. The Fe^{2+} doublets corresponding to olivine and pyroxene have areas equal to A^{olivine} and A^{pyroxene} ; (N) is the “true” amount of each species, and (C) is the “correction factor.”

$$A^{\text{olivine}} / A^{\text{pyroxene}} = C(N^{\text{olivine}} / N^{\text{pyroxene}})$$

where

$$C = [\Gamma_{\text{O1}} G(X_{\text{O1}}) f_{\text{O1}}] / [\Gamma_{\text{Px}} G(X_{\text{Px}}) f_{\text{Px}}]$$

So, the degree of correspondence between peak areas and actual Fe occupancy depends on 3 assumptions, namely that 1) the linewidths of the Fe^{2+} and Fe^{3+} peaks are the same; 2) saturation corrections are unnecessary if samples are correctly prepared as thin absorbers; and 3) the amount of recoil-free fraction for both Fe^{2+} and Fe^{3+} in those sites is the same. The equal linewidth (Γ) assumption is only reasonable in end members, but most fitting routines can allow linewidths to vary.

The saturation corrections for $G(X)$ is avoided if thin absorbers are used, as is the case in our laboratory experiments. However, for the reflectance mode spectra to be acquired on the martian surface, understanding the extent of variation of $G(X)$ will be a problem.

Recoilless fractions depend greatly on site geometries and valence state, and, thus, different values of f are likely in cases where 2 sites have radically different geometries. Fortunately, DeGrave and van Alboom (1991) have calculated (on the basis of experimental measurements of the variation in isomer shift as a function of temperature) room temperature f values for olivine, diopside, and enstatite to be 0.744, 0.708, and 0.710–0.773, respectively, so the correction factor will be only a few % of the total Fe.

In short, telling olivine and pyroxene apart is easy in a Mössbauer spectrum of a mixture, and one can quantify the

relative amounts of Fe in each phase under our laboratory conditions, provided that f values are known.

Implications for Remote Mössbauer Spectroscopy

The Mössbauer spectrometers on the Athena rovers have as their scientific goals the identification and quantification of relative amounts of Fe-bearing minerals, as well as determination of their $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios. Successful attainment of these goals will depend largely on the type of rocks found on the surface, and expectations for this depend largely on the means by which our present knowledge of martian mineralogy has been determined. Remote-sensed spectra of the martian surface suggest a predominance of pyroxene and iron oxides. For example, recent MGS TES observations (Bandfield 2002) found primarily: 1) pyroxene; 2) a material described as being either sheet silicate or high-Si glass; 3) hematite (notably at Meridiani Planum, the proposed landing site of one of the MER landers); and 4) olivine. (Plagioclase feldspar, also detected in large quantities, is not generally detectable by Mössbauer spectroscopy, due to its low iron content.) Other minerals that were detected at lower levels include basaltic glass and sulfates (Bandfield 2002). The Mössbauer parameters of hematite at Mars surface temperatures have been determined by our group and by DeGrave and van Alboom (1991), and they are quite distinct from those of pyroxene, glass, and olivine, so that hematite should easily be discriminated by the remote Mössbauer spectrometers on the MER and Beagle 2 missions. This has the exciting potential for laying to rest the ancient question of “Why is Mars red?” If the oxide phase is not hematite, we still have an excellent chance of identifying it unequivocally because the Mössbauer spectra of most oxides are quite distinctive sextets, particularly at Mars surface temperatures. Mössbauer spectra of glasses compared with sheet silicates will be more difficult to differentiate, as their parameters at Mars surface temperatures are poorly known. However, at 300K, Mössbauer spectra of glass, sheet silicates, and pyroxenes are nearly indistinguishable (compare the pyroxene data presented here versus Mössbauer data reviewed in Dyar 1985 for glasses and Dyar 2002 and Coey 1980 for micas and clay minerals). Fortunately, olivine can probably be resolved distinctly from these phases (at least, as far as is known from room temperature spectra, cf., this study and Dyar [1984]).

On the other hand, if the rocks on the surface of Mars are anything like those in the SNC meteorites, identifying and quantifying relative amounts of Fe-bearing minerals likely will be difficult. Interpretations of whole rock data are difficult because the bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ records the distribution of Fe atoms only and does not take into consideration the number of Fe atoms present in each phase. For example, a small amount of Fe oxide may contain a disproportionately large percentage of the total Fe atoms present in the sample

and, thus, have a large effect on the bulk $\%\text{Fe}^{3+}$ contents. Alternatively, if the phases that are mixed together have comparable Fe contents and molar volumes, then the difference between the observed peak areas and the mineral modes may not be so large.

As an example, consider the bulk rock spectrum of Nakhla, which has 29.1% of the Fe^{2+} in olivine and 67.3% in pyroxene. To satisfy the Athena mission goals, the mineral modes, which reflect the variations in effective volume of the phases present, must be determined. Based on the molar volumes of the unit cells of olivine ($Z = 4$, volume $\approx 290 \text{ \AA}^3$) and pyroxene ($Z = 4$, volume $\approx 449 \text{ \AA}^3$) and their known Fe contents, the predicted modal percentage of Fe atoms based on Mössbauer results should be 9.7% olivine and 90.3% pyroxene. This compares very well with the normalized observed mode of 11% olivine and 89% pyroxene. This is in a controlled situation where we are confident of the phase identifications and the Fe contents of each silicate are known and relatively constant.

What if variation exists in the chemical composition of the silicates (i.e., what if olivine and/or pyroxene are zoned?). Consider the example of LEW 88516, in which the olivine is compositionally zoned from Fo_{70} – Fo_{64} and both high-Ca and low-Ca pyroxenes are present (Harvey et al. 1993; Treiman et al. 1994). The bulk rock Mössbauer spectrum of LEW 88516 has 57.1% of the total Fe as Fe^{2+} in olivine, and 40.2% of the total Fe as Fe^{2+} in pyroxene; from this and the independently known chemical composition, a mode of 43.1% olivine and 56.9% pyroxene would be predicted. From Table 2, the actual normalized mineral mode is 12–35% pyroxene and 45–59% olivine. The discrepancy between the mode predicted by Mössbauer and the observed mode results from compositional zoning and, probably, heterogeneity in the mineral distribution in the meteorite. In this case, predicting a mineral mode from a Mössbauer spectrum is of little value.

These examples have important consequences for interpretation of data from MER, Beagle 2, and other remote Mössbauer instruments. In those situations, we will not even know the chemical composition of the constituent phases, and that will add a further source of ambiguity to the modal calculations. Essentially, calculation of mineral modes from Mössbauer spectra is (at least) a 3-variable problem: Mössbauer peak areas, total Fe contents of each phase, and mineral mode are all interrelated. If mineral modes and the Fe contents of the component phases are known, Mössbauer doublet areas can be predicted, albeit inconsistently, as the examples above show. However, this relationship does not work in reverse (i.e., in remote acquisitions) because 3 variables exist, 2 of which are unknown. Doublet areas in the Mössbauer spectrum of a mixture of minerals cannot be used to estimate modal mineralogy without known chemical compositions. In the rare cases where the bulk rock is a mixture of, say, hematite and magnetite (phases where the chemical compositions are relatively constant), modal

estimates might be confidently made based on Mössbauer spectra of mixtures. Unfortunately, in cases where the bulk rock contains silicates with variable Fe contents (i.e., nearly any silicate!) one cannot deduce modes from Mössbauer doublet areas without making unconstrained assumptions about the Fe contents of the individual phases. Interpretation of MER, Beagle 2, and other remotely acquired data for which individual phase compositions will not be known will be (regrettably) complicated by this simple constraint.

Comparison with XANES Results

Over the past decade, the determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in μm -scale areas using synchrotron micro-XANES (SmX) spectroscopic measurements of Fe pre-edge peak energies, as pioneered by Najt et al. (1994), has been successfully demonstrated and applied to a wide variety of mineral groups (Delaney et al. 1998a), including SNC meteorites (Delaney et al. 1998b; Delaney and Dyar 2000). The SmX technique uses a microbeam as small as $4 \times 4 \mu\text{m}$, making it superior to Mössbauer analyses by virtue of its spatial resolution, which is on the scale of SIMS. However, proper interpretation of SmX spectra and determination of accurate $\text{Fe}^{3+}/\Sigma\text{Fe}$ requires knowledge of grain orientation (or analysis of variably orientated grains; Dyar et al. 2002; Gunter et al. 2002) as well as mineral group-specific standards to obtain best results ($\text{Fe}^{3+}/\Sigma\text{Fe}$ values 3–5% absolute, nearly comparable to those of Mössbauer spectroscopy; Dyar et al. 1998). In situations where grain orientation cannot be controlled, the error bars on pyroxene Fe^{3+} determinations by SmX are roughly $\pm 20\%$ absolute (Dyar et al. 2002).

Delaney and Dyar (2003) compare results from SmX analyses of randomly oriented SNC pyroxene to the Mössbauer work presented here; a revised summary of that comparison, using the finalized fits presented in this paper, is given in Table 6. The results from the 2 methods agree within the error bars on both techniques. This comparison lends credibility to the XANES results and opens the way for studies of zoning of Fe^{3+} and Fe^{2+} using the SmX technique.

Effects of Shock on Fe^{3+} in SNC Minerals

As noted above, dehydrogenation, caused by shock heating and pressure, is likely to be responsible for the presence of Fe^{3+} in the olivines studied here. This raises the issue of the effects of shock on pyroxene and other phases present. Interpretation of $f\text{O}_2$ (or $f\text{H}_2$) of meteorites depends on the assumption that shock effects do not change either Fe^{3+} or H. Two aspects of this problem exist: 1) can dehydrogenation result in all the oxidation observed in pyroxene?; and 2) can shock processes reduce or oxidize Fe via interactions with the prevailing atmosphere during shock?

The answer to the first of these questions lies in thermodynamics. That some contribution from

Table 6. Comparison of SmX and Mössbauer results for pyroxene in SNC meteorites.

Meteorite	% Fe^{3+} by SmX	% Fe^{3+} by Mössbauer
ALH 84001	0	0
Nakhla	0–5	2.3
QUE 94201	8	1.7
Shergotty	11	1.7
Zagami	2	1.4

dehydrogenation processes is represented in clinopyroxene is definitely possible. Ingrin et al. (1995) have suggested that hydrogen diffusivity increases as total Fe content increases. Therefore, if hydrogen is present in SNC pyroxene before shock (as it is present in terrestrial mantle pyroxene, based on work by Rossman and coworkers, e.g., Skogby et al. [1990]; Smyth et al. [1991]) and grain size is small when sufficient Fe content is present, significant amounts of hydrogen may diffuse out of cpx as a result of shock. Thus, shock remains a possible explanation for the Fe^{3+} observed in pyroxene in this study.

In answer to the second question, a pilot project reported in Therkelsen et al. (2002) has tested the relationship between shock and oxidation/reduction. Run products of shock experiments on 2 lithologies from the layered Stillwater Complex in Montana by Johnson et al. (2001) were studied. Anorthosite (>90% An_{75} plag) and an orthopyroxenite (>90% En_{85} opx) were shocked at pressures ranging from 17 to 60 GPa under an atmosphere of air at 10^{-3} torr. Samples were analyzed for $\text{Fe}^{3+}/\Sigma\text{Fe}$ using SmX.

Results of this senior thesis project (Therkelsen 2002) were mixed. The major element compositions of feldspar, pyroxene, and olivine remained unchanged as a function of increasing shock pressure, suggesting that the temperatures involved were not high enough to either volatilize Na or diffuse other major elements. The FeO content of the feldspar is roughly constant over the range of pressures studied, so no evidence exists for the presence of a mafic component (resulting from melting of proximal olivine or pyroxene) that might indicate the presence of shock melt glass.

The percentage of total Fe present as Fe^{3+} changed little with increasing shock pressures, though the effect is different for different minerals because of their composition and steric constraints. Some indication exists of oxidation of olivine and feldspar with progressive amounts of shock, but the amount of change is within the error bars for the technique. Data collection and interpretation were frustrated by the heterogeneity of the starting materials and the presence of alteration products heterogeneously distributed in them. Furthermore, the pyroxenes in both starting rocks were exsolved to varying degrees. We did not find any of the oxidized brown olivines described by Bauer (1979) and Ostertag and Stöffler (1982), though this might have been due to the lack of thermal annealing. In short, the only experimental work to date to directly measure the potential

oxidation/reduction of pyroxene via shock is inconclusive. Further experiments to examine this effect are in progress.

Relationship between Fe^{3+} and $f\text{O}_2$

As stated at the outset, considerable interest exists in understanding the oxygen fugacity of martian magmas, because of the effect of $f\text{O}_2$ on mineral chemistry and crystallization processes. Work by McCanta and Rutherford (2002), Musselwhite and Wadhwa (2002), Wadhwa (2001), Herd (2002), and McKay et al. (1994) suggests that the $f\text{O}_2$ of SNC meteorites ranges from QUE 94201 (roughly IW + 1) to Dar al Gani, EET A79001A and B, Los Angeles, Zagami, and Shergotty (roughly IW + 1.8–3.5) in order of increasing oxidation. Over this range, there is little or no correlation of $f\text{O}_2$ and $\text{Fe}^{3+}/\Sigma\text{Fe}$. However, as pointed out by McCanta et al. (2003), these are all relatively reducing conditions. In shergottitic basalt analogues, significant Fe^{3+} does not even appear in the melt until about the NNO buffer, and the distribution of Fe^{3+} between melt and pyroxene is poorly known.

CONCLUSIONS

This study has attempted to address 3 fundamental issues involving Mössbauer spectroscopy of SNC meteorites. Summarizing the conclusions by invoking them as follows is helpful.

As a group, what do the whole rock Mössbauer spectra of SNC meteorites predict for possible Mössbauer spectra acquired on the martian surface? Mössbauer spectroscopy will be useful for mineral identifications (“fingerprinting”) in remote applications as long as the phases present have distinctive peak parameters. Fortunately, the igneous minerals likely to be present on Mars (as represented by SNCs) have a relatively limited range of likely Fe-bearing mineralogies, and the peak positions of Fe oxides lie largely outside the velocity range of silicate peaks. Discriminating between olivine and pyroxene will be relatively easy, and distinguishing low-Ca and high-Ca pyroxene will be very difficult. If mixtures of oxides with these silicates are present on Mars, Mössbauer results should place useful constraints on phase identification, though this capability may be limited if nanophase oxides are present (Morris et al. 1989) because their peaks lie in the same velocity ranges of those from silicates.

How are the whole rock spectra related to the spectra of mineral separates, and what can (and cannot) be learned from whole rock spectra about the Fe^{3+} composition and identities of individual minerals? The data presented here demonstrate experimentally what is already known theoretically: the fact that mineral modes cannot be obtained from Mössbauer spectra of bulk rocks unless the Fe contents of the individual phases are known. This reality imposes significant constraints

on Mössbauer spectrometers on remote landers because, in most cases (i.e., when any rock containing silicate is analyzed), data interpretation will be limited to phase identification rather than quantification. Generally, identifying which of the paramagnetic phases present has Fe^{3+} , if any, will not be possible.

How are the Fe^{3+} contents of the minerals in the SNCs related to the oxygen fugacity of the magmas from which they formed? In this data set, no relationship exists between Fe^{3+} content and $f\text{O}_2$. Possibly, all of the Fe^{3+} observed in olivine is the result of dehydrogenation rather than oxidation, and this process may also be the source of all the Fe^{3+} observed in pyroxene. Also, likely, the observed Fe^{3+} in pyroxene records an equilibrium between pyroxene and melt at such low $f\text{O}_2$ that little or no Fe^{3+} would be expected (McCanta et al. 2003). At the present time, not enough experimental or empirical data exists to draw any substantive conclusion about this relationship. Additional experimental work is needed to address this important question.

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