

MÖSSBAUER SPECTROSCOPY OF MINERAL SEPARATES FROM SNC METEORITES. M. D. Dyar¹
¹Department of Astronomy, Kendade Hall, Mount Holyoke College, 50 College St, South Hadley, MA 01075; mdyar@mtholyoke.edu.

Introduction: Numerous workers have recently focused attention on the issue of the oxygen fugacity (f_{O_2}) of martian samples [1,2,3,4,5]. Estimates of f_{O_2} based on Fe-Ti oxides [6] and D_{Eu}/D_{Gd} and D_{Eu}/D_{Sm} ratios [3,4,7] suggest a range of f_{O_2} values for SNC meteorites from IW+2.5 - IW+3.5 for Shergotty to IW-2.0 - IW+0.2 for QUE94201 [3,4]. Fe^{3+}/Fe^{2+} is also a function of f_{O_2} , and synchrotron micro-XANES values for olivine, pyroxene, and feldspar Fe^{3+} have been reported in [8,9]. However, the relationship between the reported Fe^{3+} values and the other methods for estimating f_{O_2} is not clear, and further measurements of Fe^{3+}/Fe^{2+} by a more conventional technique have been needed. Accordingly, in this project, new Mössbauer spectroscopy data on mineral separates handpicked from 10 SNC meteorites are reported.

Previous Work: Previous work on these meteorites is summarized in Table 1. The only workers to extract and analyze mineral separates were Ostertag et al. (olivine) [20, 21], Vieira et al. [22], and Vistisen [23] (pyroxene), and these data show only very small percentages of Fe^{3+} in olivine and pyroxene. However, none of the previous workers has related the $Fe^{3+}/\Sigma Fe$ of the bulk separates to the Fe contents and modes of individual minerals present, so $Fe^{3+}/\Sigma Fe$ ratios of individual phases could not be assessed.

Table 1. Mössbauer Spectroscopy of SNC Samples

Meteorite	Analysis	% Fe^{3+}
ALHA 77005	WR [10, 11, 14]	1.7-1.8
	olivine separate [20, 21]	4.5
Chassigny	WR [12, 13, 14]	2.3
EETA 79001	WR [10, 14, 15]	0.5-1.9
Governador Valadares	WR [14, 15]	n.s.
Lafayette	WR [14, 15]	n.s.
Nakhla	WR [10, 14, 15, 17, 22]	1.6
	pyroxene separate [23]	2.0
Shergotty	WR [14, 15]	n.s.
Zagami	WR [14-17, 19, 22]	n.s.
	pyroxene separate [22]	<1.0

WR = whole rock analysis, n.s. = not specified.

Methods: In the current study, roughly 200 mg samples of each of 10 SNC meteorites were obtained from JSC, NMNH, and the Vatican (Table 2). A 10-20 mg chip of each sample was set aside for whole rock MS (as reported in [24]), and the remaining mass was crushed to allow handpicking of mineral separates for phases constituting more than 30% of the mode. Gray

cells in Table 2 indicate phases for which separates were prepared by handpicking under a binocular microscope. Sample masses ranged from 1.5-34 mg. All separates were sent to RELAB for FTIR, reflectance, and emission spectra before Mössbauer mounts were prepared; those results will be reported elsewhere.

Table 2. Mineral Modes (%) for Samples Studied

Meteorite	Px	Fsp*	OI	Ox	#	Ref.
ALHA 77005	35	8	50			[25]
ALHA 84001	97	1		2		[26]
Chassigny	5	2	92	1		[27]
LEW 88516	35	8	50		5	[28]
Los Angeles	40	45	3	3	9	[29]
Nakhla	80		10		10	[30]
QUE 94201	44	46		2	8	[31]
Shergotty	70	24		2	4	[32]
Zagami	70	24		3	3	[33]
EETA 79001	70	17	9	3	1	[34]

*Fsp or maskelynite, # = other phases such as glass

For all Mössbauer analyses, samples were then gently crushed under acetone to a fine powder, mixed with sucrose to avoid preferred orientation, and run on a WEB Research spectrometer at 300K. Data were processed using the WMOSS software package, which allows use of multiple models for line shape. Quadrupole splitting distributions were used for all fits following the method of [35]. Errors on peak areas are estimated to be $\pm 1-3\%$ absolute, so most Fe^{3+} contents in these samples are right at our detection limits; this was also the case for previous studies.

Results: Mössbauer data are shown grouped by mineral species in Figures 1 and 2. Approximate Fe^{3+} contents (relative to total Fe atoms) in olivines range from 0% in Chassigny, to 3% in Nakhla and ALHA 77005, and 8-22% on two different separates from EETA 79001. For pyroxene, Fe^{3+} ranges from 0 in ALHA 84001 up to 3% in Nakhla and Los Angeles. These results are comparable to Fe^{3+} values measured by XANES (within the $\pm 10-20\%$ error bars on that technique), both in SNC meteorites [8,9] and in experimental analogs [36].

Comparisons with whole rock data are difficult because the bulk $Fe^{3+}/\Sigma Fe$ records the distribution of Fe atoms only, and does not take into consideration the number of Fe atoms in each phase that is present. 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 %Fe³⁺ contents. However, it is possible to calculate the predicted bulk sample %Fe³⁺ based on knowledge of the mineral modes (Table 2), unit cell volumes, and the %Fe³⁺ of each phase. When this calculation is performed, our results on mineral separates are in excellent agreement with previous studies of bulk samples.

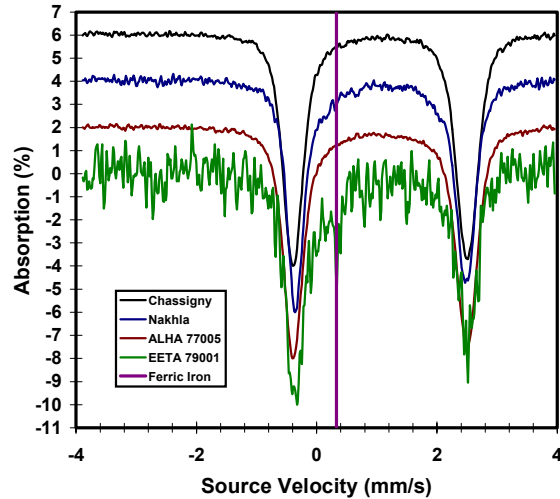


Figure 1. Mössbauer spectra of olivine separates from SNC meteorites, arranged in order from most reduced at the top to most oxidized at the bottom. Vertical line indicates centroid of the upper velocity Fe³⁺ peak.

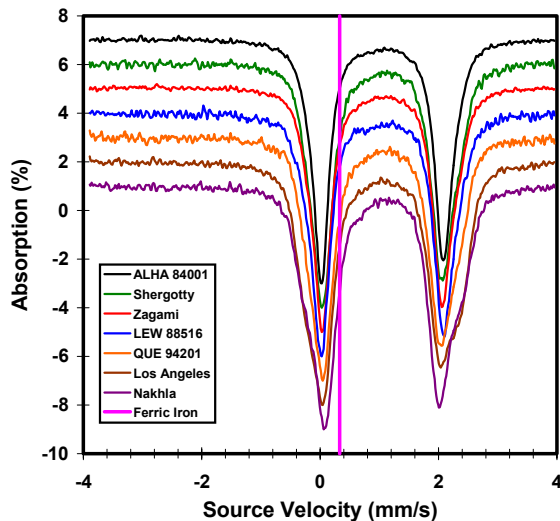


Figure 2. Mössbauer spectra of pyroxene separates from SNC meteorites, arranged in order from most reduced at the top to most oxidized at the bottom. Vertical line indicates centroid of the upper velocity Fe³⁺ peak.

Discussion: Unfortunately, the partitioning of Fe³⁺ among silicates, glass, and oxides is poorly known for any f_{O_2} , so it is impossible to specify an f_{O_2} with which

the minerals studied here might be in equilibrium. It is also worth noting that composition has an effect on the ability of a mineral to incorporate Fe³⁺. For example, it is well-known that low-Ca pyroxenes can only accommodate a small amount of Fe³⁺ [37]. Thus, the Fe³⁺/ΣFe content of any phase can only be a function of f_{O_2} if steric constraints allow Fe²⁺-Fe³⁺ substitutions to occur (see also [36]).

Another interesting aspect of this data set is the fact that ordering in pyroxene can be used to determine cooling rates of rocks and meteorites [e.g. 38]. We are investigating the relationship between Fe²⁺-Mg order-disorder and shock histories in the meteorites studied.

Finally, this work demonstrates that a state-of-the-art Mössbauer spectrometer specifically tuned to analyze small samples can acquire high-quality data on samples as small as 1.5 mg. This work opens the door for future studies of individual mineral phases from complex meteorites.

Acknowledgments: NASA grants NAG5-10424 and NAG5-12687. I also thank Gerard J. Marchand for his amazing handpicking of these very tiny samples.

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