Mössbauer study of Meridiani Planum, the first iron-nickel meteorite found on the surface of Mars by the MER Opportunity

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Abstract–Meridiani Planum is the first iron meteorite found on Mars. It was discovered in 2005 by the Mars Exploration Rover Opportunity (MER-B). Mössbauer spectra (MS) of the unbrushed and brushed meteorite species were acquired in 10 degrees temperature windows in the range of 210–260 K. Earlier examinations of these MS have led to the conclusion that the meteorite, which contains ~7 wt% Ni, belongs to the IAB meteorite group. Here, making use of a recently developed calibration/ folding procedure for MER MS, we report the results of the MS analyses for the single temperature windows m5 (210–220 K), m6 (220–230 K), m7 (230–240 K), and m89 (240–260 K). All spectra consist of a sextet and a ferric doublet. The hyperfine field of the sextet, extrapolated to room temperature, is ~34.5 T, which is, based on Mössbauer studies of meteorites found on Earth, indeed consistent with the presence of kamacite. The fractional spectral area of the sextet is ~0.96 of the total spectrum. The ferric doublet has an average quadrupole splitting of 0.70 mm/s and is not diagnostic of any specific Fe mineral.

INTRODUCTION

On January 4 and 25, 2004, the Mars Exploration Rovers (MER) Spirit (MER-A) and Opportunity (MER-B), respectively, landed on Mars. Their goal has been to investigate Martian geology and climate, and to search for clues as to whether biological activity could have been developed during the planet's history. Both MERs carry a number of experimental devices including Mössbauer Spectrometer, the Alpha Proton X-Ray Spectrometer (APXS), the Microscopic Imager, Panoramic Camera (Pancam), and the Mini-Thermal Emission Spectrometer (Mini-TES). It is well known that Mössbauer spectroscopy (MS) offers several advantages in studying iron-containing compounds, producing results that are extremely sensitive to their electronic, magnetic, and structural properties. As such, it is a powerful tool for phase identification and quantitative phase analysis of admixtures of different Fe phases. A large number of Martian rock and soil targets have so far been probed by the so-called MIMOS II Mössbauer spectrometers (Klingelhöfer et al. 2003). The raw data of the spectra can be downloaded from a number of websites (http://ak-guetlich.chemie.uni-mainz.de/ klingelhoefer; http://anserver1.eprsl.wustl.edu; http:// pds.jpl.nasa.gov).

Iron meteorites (Solberg et al. 1989; Petersen et al. 1977; Scorzelli 1991; Christiansen et al. 1984) contain at least

5 wt% Ni. The iron-nickel alloy phases present in these meteorites are designated as kamacite or taenite, depending on the relative amounts of iron and nickel. Kamacite (α -phase) is essentially metallic iron with up to 7.5 wt% nickel in solid solution. It has a body-centered cubic structure. Taenite (γ -phase) is a face-centered cubic iron-nickel alloy with more than 25 wt% nickel in solid solution.

On January 5, 2005, MER-B ran across a small, basketball-sized rock (~30 cm across) that seemed to be a meteorite (Fig. 1) (Rodionov et al. 2005; Schröder et al. 2006; Yen et al. 2005). It has been named Meridiani Planum. Other names, such as Spongebob or Heat Shield Rock, have been used in the literature. Meridiani Planum is the first iron-nickel meteorite identified on another body in the solar system. Meteorites from Mars may represent a different "sampling" of meteorite populations in space and time, and thus give us new insight into the origins of specific types of meteorites. From the well-preserved shape and form of cuspate marks and "thumb-print"-like cavities, it is possible to say something about the velocity and atmospheric effects that this meteorite experienced during the fall. How fast the meteorite struck Mars and just how thick the Martian atmosphere was during its fall are difficult questions to answer (Bland et al. 2000; Chappelow et al. 2005). It could be a single-incident meteoroid that was slowed down on entry by a higher-density Martian atmosphere than the present one and soft-landed onto



Fig. 1. Opportunity's instrument deployment device examining Meridiani Planum (NASA/Jet Propulsion Laboratory. Left front hazard camera non-linearized downsampled EDR acquired on sol 349 of Opportunity's mission to Meridiani Planum. October 15, 2006.).

Table 1. Sol numbers of spectra and temperature windows considered in this report.

Sol number	Temperature windows ^a	
347–348 348	m5, m6, m7, m89 m5, m6, m7, m89	Measurements of the unbrushed part
350–351 351	m5, m6, m7, m89 m5, m6, m7, m89	Measurements of the brushed part

^am5: 210–220 K; m6: 220–230 K; m7: 230–240 K; m89: 240–60 K.

the surface (Chappelow et al. 2006), or it could have landed from the west with a very low difference in velocity (such as the Hoba meteorite in Namibia).

Meridiani Planum was examined by the Microscopic Imager, the MIMOS II Mössbauer spectrometer, and the APXS element analyzer. It was determined from the latter experiment that the rock is predominantly composed of Fe and Ni (Rodionov et al. 2005; Yen et al. 2005, 2006; Squyres et al. 2006), with the Ni content found to be ~7 wt%. A small area of the rock's surface was brushed with the Rock Abrasion Tool and subsequently examined again by the aforementioned instruments. Hence, two sets of experimental data are available-one for the unbrushed target (sols 347-348 and 348) and another for the brushed target (sols 350-351 and 351) (Table 1). The integral Mössbauer spectrum obtained after summing up the spectra acquired by the MIMOS II in the temperature windows m5 (210-220 K), m6 (220-230 K), m7 (230-240 K), and m89 (240-260 K), was analyzed previously by Morris et al. (2006). The authors found a hyperfine field of 34.6 T.

The present contribution reports on a deeper analysis of the individual Mössbauer spectra obtained for the four temperature windows referred to above. For each of these, the data referring to Martian sols 347-348 and 348 (see Table 1 for specifications) were summed. Only spectra posted for the two 14.4 keV channels have been considered. Calibration of the measurements was performed using a novel procedure we developed and proven to yield reliable and consistent Mössbauer parameter values, as will be presented in a forthcoming paper. Eight reference channels, six from the α -Fe and two from the most prominent outer lines of the hematite component, were obtained for each half of the spectrum by fitting well-chosen parts of the spectra of the internal reference absorber with individual Lorentzian functions. The corresponding velocity values were calculated from the hyperfine parameters derived from MS of a laboratory reference target. Polynomials of the second and third order are fitted to eight experimental data sets. The two two-column files of the calibrated left and right halves for this spectrum were then joined together one after the other, and the velocities and corresponding counts were subsequently ordered in ascending velocity sequence. Finally, counts of two successive channels were added together and the respective velocities were averaged. With this method it was possible to establish single-temperature window analyses of the sample.

The calibrated and folded MS of the meteorite target are composed of a sharp well-defined sextet that can be attributed to a metallic iron phase, and a weak doublet that so far could



Fig. 2. Mössbauer spectra of unbrushed Meridiani Planum meteorite collected in the temperature windows m5 (210-220 K), m6 (220-230 K), m7 (230-240 K), and m89 (240-260 K). All spectra consist of a kamacite sextet and a weak ferric doublet (filled).

not be assigned to any specific phase (Fig. 2). Both sextet and doublet were adjusted with symmetrical Lorentzian-shaped line profiles. Some restrictions were imposed in the fitting procedure of the iron sextet, i.e., two width parameters were used (intrinsic width Γ and broadening parameters $\Delta\Gamma$) and the quadrupole shift $2\epsilon_Q$ was forced to be zero. For the spectrum acquired in window m6 (220-230 K), it was found necessary to fix the isomer shift at zero. No constraints were enforced for the relative spectral areas of the sextet lines (Table 2).

To resolve the weak doublet component from the composed spectrum, constraints had to be imposed on its hyperfine parameters. Generally the hyperfine parameters for a paramagnetic Fe³⁺ doublet do not change significantly when increasing the measuring temperature from 210 K to 260 K, particularly when the object and reference target reside at the same temperature. Based on numerous trial fits, the isomer shift δ , the quadrupole splitting ΔE_Q , and line width Γ for the doublet were eventually fixed at values of 0.36 mm/s, 0.70 mm/s, and 0.41 mm/s, respectively, which are all characteristic for ferric species in an octahedral O₆ or (O,OH)₆ coordination. Possibly, this doublet component corresponds to an Fe phase resulting from oxidation.

Table 2. Relevant Mössbauer parameters of the sextet and the doublet component present in the spectra acquired for the unbrushed Meridiani Planum in the temperature windows m5, m6, m7, and m89^a.

	Sextet		Doublet			
Temperature	B_{hf}	δ ^b	Sc	δ ^b	ΔE_Q	Sc
window	(T)	(mm/s)		(mm/s)	(mm/s)	
m89	34.7	-0.01	0.96	0.36 ^d	0.70 ^d	0.04
m7	34.8	-0.02	0.96	0.36 ^d	0.70	0.04
m6	34.6	0.00 ^d	0.96	0.36 ^d	0.70 ^d	0.04
m5	34.9	-0.01	0.96	0.36 ^d	0.69	0.04

^aMB parameter errors are 0.02 mm/s for δ and ΔE_O and 0.5 T for B_{hf} . ^bReferred to α -Fe at the same temperature of the measurement. ^cFractional spectral area of total spectrum. ^dParameter value fixed in the iteration.

Table 3. Relevant Mössbauer parameters of the sextet and the doublet component present in the spectra acquired for the Meridiani Planum after brushing in the temperature windows m5, m6, m7, and m89^a

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	Sextet		Doublet						
Temperature	B_{hf}	δ ^b	S^{c}	δ^{b}	ΔE_Q	Sc			
window	(T)	(mm/s)		(mm/s)	(mm/s)				
m89	34.4	-0.02	0.94	0.34	0.73	0.06			
m7	34.5	0.00	0.95	0.36 ^d	0.74 ^d	0.05			
m6	34.3	0.01	0.91	0.34	0.75	0.09			
m5	34.4	0.00	0.94	0.36 ^d	0.78	0.06			

^aMB parameter errors are 0.02 mm/s for δ and ΔE_Q and 0.5 T for B_{hf} . ^bReferred to α-Fe at the same temperature of the measurement. ^cFractional spectral area of total spectrum.

^dParameter value fixed in the iteration.

The derived isomer shifts of the sextets are in excellent agreement with the known results for pure metallic iron at identical temperatures. On the other hand, the hyperfine field values, e.g., 34.7 T at an average temperature of ~215 K for window m5, are significantly higher by an amount of ~1.3 T as compared to the field of pure α -Fe at the same temperature. This finding is consistent with the presence of Ni in the α -Fe structure, as suggested by the in situ MER APXS analysis of the meteorite target and with the conclusion put forward by Morris et al. (2006). It is also consistent with data for the ironnickel meteorite Soledade, which has a Ni concentration of 6.8 wt%, and for which a hyperfine field of 34.4 T at room temperature (Paduani et al. 2005) was measured. This value is higher by about 1.4 T compared to the hyperfine field that is typical for α -Fe at room temperature, i.e., 33.0 T.

It is observed that the Fe-Ni sextet lines exhibit significant broadening. On average, the width parameters are adjusted to be $\Gamma = 0.33$ mm/s and $\Delta\Gamma = 0.10$, compared with 0.32 mm/s and ~0.04, respectively, for the α -Fe component in the spectrum of the reference target. This line broadening may be attributed to a small distribution in hyperfine fields (spread of ~ 1 T), probably due to the variation in the number of Ni atoms surrounding the Fe atoms. Finally, it is



Fig. 3. The Mössbauer spectrum of the brushed part of Meridiani Planum for the temperature window m6 (220–230 K). The spectrum consist of a kamacite sextet and a weak ferric doublet (filled).

worthwhile to mention that the area ratios of the outer to middle to inner lines are consistently 3:1.2:1. The considerable deviation from the ideal 3:2:1 ratios for a random spin orientation in the target material may indicate a preferential orientation of the magnetic moments with respect to the target's surface.

The results of the Mössbauer analyses for the brushed part of Meridiani Planum are listed in Table 3. For each temperature window, two spectra, acquired on sols 350–351 and sol 351, respectively, were taken into account and processed in a manner similar to those of the unbrushed target. A typical spectrum is shown in Fig. 3 for the temperature window m6. From Tables 2 and 3, it is clear that the Mössbauer parameters for the brushed and unbrushed surface of the meteorite species are very similar. There might be a tendency for the hyperfine field to be lower by about 0.3 T and for the fractional doublet contribution to be higher by about 0.03 for the target after being brushed, however, this suggestion must be regarded with necessary reserve.

According to Zhang et al. (1994), it has been established that in Fe-Ni alloys an increase of the Ni content from 0 to 20 wt% (kamacite) slightly increases the magnetic hyperfine field. Values for the hyperfine field of kamacite at room temperature (RT), as reported in Mössbauer studies of various meteorites (Abdu et al. 1997; Böttger et al. 1997; Grokhovsky et al. 2005; Oshtrath et al. 2004; McCammon 1995), are plotted as a function of the nickel content in Fig. 4, which clearly demonstrates above-mentioned correlation. Since Meridiani Planum was not measured at RT, the RT hyperfine field of the Fe-Ni sextet is unknown. An extrapolation to RT of the values shown in Table 3 yields an estimated value of 34.5 T (star in Fig. 4). Based on this value and on the small nickel amount (7 wt%) as measured for the Meridiani Planum, the authors conclude the iron sextet to be due to



Fig. 4. The hyperfine field of kamacites in meteorites that have been found on Earth as function of the nickel content. With a further increase (above 20 wt%) of the Ni content, the Fe-Ni alloy forms taenite and the magnetic field further decreases with increasing wt% of Ni (Abdu et al. 1997; Böttger et al. 1997; Grokhovsky et al. 2005; Oshtrath et al. 2004; McCammon 1995).

kamacite. Pure kamacite forms cubic crystals with six equal sides at rights angles to each other.

Earlier, Meridiani Planum has been formally classified as an IAB complex (Yen et al. 2006; Connolly et al. 2006) based on the concentration of trace elements. Mössbauer hyperfine parameters have been published by Morris et al. (2006) for a temperature range of 210-270 K. In this paper, Mössbauer analysis of the meteorite has been performed for single temperature (10 K) windows. The dominant sextet shows a large texture effect, which has been overlooked by earlier workers on this meteorite's MS. It is proven to be due to kamacite by comparison of its hyperfine parameters with those of meteorites found on Earth. The amount of nickel in Meridiani Planum is 7 wt%, which is close to the ~6 wt% that is commonly considered as the upper limit for hexahedrites. No indication has been found for the presence of taenite (which possesses a significantly different hyperfine field [~30.0 T] as compared to kamacite, approximately 34.5 T), which should be present for a classification as an octahedrite, thus favoring its classification as a hexahedrite.

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REFERENCES

Abdu Y. A. and Ericsson T. 1997. Mössbauer spectroscopy, X-ray diffraction, and electron microprobe analysis of the New Halfa meteorite. *Meteoritics & Planetary Science* 32:373–375.

- Böttger C., Campbell S. J., Wu E., and Smith R. G. 1994. Mössbauer and X-ray studies of an iron meteorite sample. *Hyperfine Interactions* 91:563–569.
- Bland P. A. and Smith T. B. 2000. Meteorite accumulations on Mars. *Icarus* 144:21–26.
- Chappelow J. E. and Sharpton V. L. 2005. Influences of atmospheric variations on Mars's record of small craters. *Icarus* 178:40–55.
- Chappelow J. E. and Sharpton V. L. 2006. The event that produced Heat Shield Rock and its implications for the Martian atmosphere. *Geophysical Research Letters* 33:L19201.
- Christiansen A., Larsen L., Roy-Poulsen H., Roy-Poulsen N. O., and Vistisen L. 1984. Iron-nickel alloys in a taenite lamella from the iron meteorite Cape York as measured by conversion electron Mössbauer spectroscopy. *Physica Scripta* 29:94–96.
- Connolly H. C. Jr., Zipfel J., Grossman J. N., Folco L., Smith C., Jones R. H., Righter K., Zolensky M., Russell S. S., Benedix G. K., Yamaguchi A., and Cohen B. A. 2006. The Meteoritical Bulletin, No. 90. *Meteoritics & Planetary Science* 41:1383– 1418.
- Grokhovsky V. I., Oshtrath M. I., Milder O. B., Semionkin V. A., Kadushnikov R. M., and Glaskova S. A. 2005. Structural studies of iron meteorite Dronino (abstract #1980). 36th Annual Lunar and Planetary Science Conference. CD-ROM.
- Klingelhöfer G., Morris R. V., Bernhardt B., Rodionov D., de Souza P. A., Squyres S. W., Foh J., Kankeleit E., Bonnes U., Gellert R., Schröder C., Linkin S., Evlanov E., Zubkov B., and Prilutski O. 2003. Athena MIMOS II Mössbauer spectrometer investigation. *Journal of Geophysical Research* 108:8067–8084.
- McCammon C. 1995. Mössbauer spectroscopy of minerals. In Mineral physics & crystallography: A handbook of physical constants, edited by Ahrens T. J. Washington, D.C.: American Geophysical Union. pp. 332–347.
- Morris R.V., Klingelhöfer G., Schröder C., Rodionov D. S., Yen A., Ming D. W., de Souza P. A. Jr., Wdowiak T., Fleischer I., Gellert R., Bernhardt B., Bonnes U., Cohen B. A., Evlanov E. N., Foh J., Gütlich P., Kankeleit E., McCoy T., Mittlefehldt D. W., Renz F., Schmidt M. E., Zubkov B., Squyres S. W., and Arvidson R. E. 2006. Mössbauer mineralogy of rock, soil, and dust at Meridiani Planum, Mars: Opportunity's journey across sulfaterich outcrop, basaltic sand and dust, and hematite lag deposits. *Journal of Geophysical Research* 111:E12S15.
- Oshtrath M. I., Milder O. B., Grokhovsky V. I., and Semionkin V. A. 2004. Hyperfine interactions in iron meteorites: Comparative study by Mössbauer spectroscopy. *Hyperfine Interactions* 158: 365–370.
- Paduani C., Perez C. A. S., and Ardisson J. D. 2005. A Mössbauer effect study of the Soledade meteorite. *Brazilian Journal of Physics* 35:667–669.
- Petersen J. F., Aydin M., and Knudsen J. M. 1977. Mössbauer spectroscopy of an ordered phase (superstructure) of FeNi in an iron meteorite. *Physics Letters* 62A:192–194.

- Rodionov D. S., Klingelhöfer G., Ming D. W., Morris R. V., Schröder C., de Souza J. P. A., Squyres S. W., and Yen A. S. 2005. An iron-nickel meteorite on Meridiani Planum: Observations by MER Opportunity's Mössbauer spectrometer (abstract #10242). *Geophysical Research Abstracts* 7.
- Schröder C., Gellert R., Jolliff B. L., Klingelhöfer G., McCoy T. J., Morris R. V., Rodionov D. S., de Souza P. A., Yen A. S., Zipfel J., and the Athena Science Team. 2006. A stony meteorite discovered by the Mars Exploration Rover Opportunity on Meridiani Planum, Mars (abstract). *Meteoritics & Planetary Science* 41:A160.
- Scorzelli R. B. 1991. Application of the Mössbauer effect to the study of meteorites—A review. *Hyperfine Interactions* 66:249–258.
- Solberg T. C. and Burns R. G. 1989. Iron Mössbauer spectral study of weathered Antarctic and SNC meteorites. Proceedings, 19th Annual Lunar and Planetary Science Conference. pp. 313–322.
- Squyres S. W., Arvidson R. E., Bollen D., Bell J. F. III, Brückner J., Cabrol N. A., Calvin W. M., Carr M. H., Christensen P. R., Clark B. C., Crumpler L., Des Marais D. J., d'Uston C., Economou T., Farmer J., Farrand W. H., Folkner W., Gellert R., Glotch T. D., Golombek M., Gorevan S., Grant J. A., Greeley R., Grotzinger J., Herkenhoff K. E., Hviid S., Johnson J. R., Klingelhöfer G., Knoll A. H., Landis G., Lemmon M., Li R., Madsen M. B., Malin M. C., McLennan S. M., McSween H. Y. Jr., Ming D. W., Moersch J., Morris R. V., Parker T., Rice J. W. Jr., Richter L., Rieder R., Schröder C., Sims M., Smith M., Smith P., Soderblom L. A., Sullivan R., Tosca N. J., Wänke H., Wdowiak T., Wolff M., and Yen A. 2006. Overview of the Opportunity Mars Exploration Rover mission to Meridiani Planum: Eagle crater to Purgatory Ripple. Journal of Geophysical Research 111:E12S12.
- Van Cromphaut C., De Resende V. G., De Grave E., Van Alboom A., Vandenberghe R. E., and Klingelhöfer G. 2007. Characterisation of the magnetic iron phases in Clovis Class rocks in Gusev crater from the MER Spirit Mössbauer spectrometer. *Geochimica et Cosmochimica Acta* 71:4814–4822.
- Yen A. S., Gellert R., Zipfel J., Economou T., McLennan S., Schröder C., and the Athena Science Team. 2005. Meteoritic contributions to the surface of Mars (abstract #09861). *Geophysical Research Abstracts* 7.
- Yen A. S., Mittlefehldt D. W., McLennan S. M., Gellert R., Bell J. F., McSween H. Y. Jr., Ming D. W., McCoy T. J., Morris R. V., Golombek M., Economou T., Madsen M. B., Wdowiak T., Clark B. C., Jolliff B. L., Schröder C., Brückner J., Zipfel J., and Squyres S. W. 2005. Nickel on Mars: Constraints on meteoritic material at the surface. 2006. *Journal of Geophysical Research* 111:E12S11.
- Zhang Y. C., Stevens J. G., Li Y. S., and Li Z. L. 1994. Mössbauer study of the Jilin and Xinyang meteorites. *Hyperfine Interactions* 91:547–550.