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# Mineralogical analysis of Martian soil and rock by a miniaturized backscattering Mössbauer spectrometer

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**Abstract.** The general scientific objectives of an in situ experiment employing a Mössbauer spectrometer on a Martian lander are, for both rock and soil samples, identification and relative abundance of iron-bearing minerals (including carbonates, phyllosilicates (clays), hydroxyoxides, phosphates, oxides, silicates, sulfides, sulfates), measurement of the ferric (Fe<sup>3+</sup>) to ferrous (Fe<sup>2+</sup>) ratio, determination of the properties of magnetic phases including the size distribution of magnetic particles (nanophase versus larger particles) in the Martian soil. These data provide information about the nature and extent of atmosphere-surface chemical and physical weathering processes involving Fe-bearing phases. These objectives are directly relevant to studying the evolution of volatiles and climate over time on Mars because surface materials are major volatile sinks. In fact one of the major problems associated with understanding the evolution of volatiles on Mars is understanding the processes in the past and/or present that are responsible for oxidizing the red planet. A miniaturized backscattering Mössbauer spectrometer, developed at the Technical University of Darmstadt, is reported on which is a flight prototype of an instrument that could be used for in situ analysis as part of a payload of a Martian lander. Its critical instrument parameters are <300 g mass, 250 cm<sup>3</sup> volume, about 0.4 W power, and about 300 mCi (at launch) <sup>57</sup>Co radiation source. Results of test measurements on Mars sample analogues will be presented. As an example for laboratory weathering studies on Fe-bearing phases, which are important for analysis and interpretation of returned data from Mars, first results of the study of weathering of basalt under CO<sub>2</sub> and CO<sub>2</sub>-O<sub>2</sub> atmospheres will be presented and discussed. Copyright © 1996 Elsevier Science Ltd

#### Introduction: Fe-Mössbauer spectroscopy on Mars

Iron Mössbauer spectroscopy (FeMS) has been used in Earth-based laboratories to study the mineralogy of ironbearing phases in a variety of planetary samples, including lunar samples returned to Earth by American Apollo astronauts and Soviet robotic missions, and meteorites that have asteroidal and Martian origins (Burns and Martinez, 1991; Fernandez-Moran et al., 1970; Gay et al., 1970; Hafner, 1975; Herzenberg and Riley, 1970; Madsen et al., 1988, 1990, 1992; Muir et al., 1970; Solberg and Burns, 1989; Wdowiak and Agresti, 1984). A variety of terrestrial samples that are spectral analogues of Martian bright regions have also been studied (e.g. Bell et al., 1993; Golden et al., 1993; Klingelhöfer et al., 1996; Morris et al., 1985, 1989a, 1993; Singer, 1982) by FeMS. To date, no in situ FeMS measurements have been made as part of any planetary mission. This situation will likely change in the future because of (1) recognition of the utility of the technique for mineralogical analyses on planetary surfaces, (2) development at the Technische Hochschule Darmstadt of protoflight backscatter Mössbauer spectrometers (Evlanov et al., 1991; Kankeleit et al., 1994; Klingelhöfer et al., 1992a, 1995) and in the U.S.A. (Agresti et al., 1990, 1992; Morris et al., 1989; Shelfer et al., 1991, 1995), and (3) inclusion of Mössbauer spectrometers in proposals for scientific instrument payloads on lunar (American Discovery) and Martian (Russian Mars-96 and American Surveyor) lander missions. Mössbauer spectrometers are also under discussion for other planetary missions (e.g. Venus and a comet rendezvous mission).

The scientific basis for landing a Mössbauer spec-

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trometer on Mars is extensively discussed by Knudsen (Knudsen, 1989; Knudsen et al., 1990, 1992). Briefly, a Mössbauer spectrometer on a Martian lander can identify and measure the relative abundance of iron-bearing minerals (e.g. carbonates, phyllosilicates, hydroxyoxides, phosphates, oxides, silicates, sulfides, sulfates), including those that are magnetically ordered, measurement of the ferric (Fe<sup>3+</sup>) to ferrous (Fe<sup>2+</sup>) ratio, and the size distribution of magnetically-ordered particles (i.e. nanophase or superparamagnetic particles versus multidomain particles). These data characterize the present state of Martian surface materials and thus provide constraints on weathering processes by which the surface evolved to its present state. FeMS can, for example, identify primary igneous mineralogies such as iron-bearing olivine and pyroxene and weathering products which do (e.g. goethite and jarosite) and do not (e.g. hematite and maghemite) contain volatiles as a part of their structures. Iron-bearing sulfides (e.g. pyrite and phyrrhotite) and carbonates (e.g. siderite) can also be detected. By determining the size distribution of oxide particles, Mössbauer analyses can differentiate between low-temperature (e.g. palagonitization) and high-temperature (e.g. oxidative alteration in an impact melt) hydrothermal processes. Another question is whether the SNC meteorites can be related to actual materials on Mars. Mössbauer spectroscopy can contribute significantly to answering this question by comparing the laboratory Mössbauer results on SNC meteorites with the data from the *in situ* analysis on Mars.

In this paper, we will consider the technical design of a flight-qualified backscatter Mössbauer spectrometer, which could be included on the landers of the Inter-MarsNet mission, and will demonstrate the performance of a protoflight instrument (MIMOS, miniaturized Mössbauer spectrometer) for analysing Martian analogue samples (a palagonite and an impactite). Furthermore, first results of laboratory studies of weathering of basalt will be presented as an example demonstrating the importance of such work for the analysis and interpretation of future Mössbauer spectra from Mars, and their relevance for the understanding of the evolution of volatiles and climate over time on Mars.

# General design of a space qualified Mössbauer spectrometer

Spacecraft missions that put landers on planetary surfaces have limited resources in mass, volume and electrical power. Because of these constraints the standard laboratory Mössbauer spectrometer had to be extremely miniaturized and optimized for power consumption and detection efficiency. All components have to withstand high acceleration forces and shocks, as well as temperature variations and cosmic ray irradiation. Because of restrictions in data transfer rates, most of the instrument functions and data processing were required to be internal to the instrument. High detection efficiency is extremely important in order to minimize experiment time. Instrument calibration could be accomplished either by a second, less intense radioactive source mounted on top of

the drive and a reference absorber in transmission geometry, or by targets with known composition mounted on the lander. Because no sample preparation is required, backscatter geometry is the measurement geometry of choice in planetary applications.

The main parts of the Mössbauer (MB) spectrometer are the electromechanical vibrator, mounted in the centre of the instrument, the <sup>57</sup>Co FeMS source, a multilayered radiation shield, the detector system, and the electronics for detector, vibrator and instrument control and data processing. The general design of these components suitable for space applications is described next.

### Mössbauer source and shielding

The highest possible source activity is desirable, with the constraint that the source line width should not increase significantly (a factor of 2–3) over the 1–3 year duration of the mission. Calculations indicate an optimum specific activity for  $^{57}\text{Co}$  at 1 Ci cm $^{-2}$  (Gummer, 1988; Evlanov et al., 1993). Sources of 150–300 mCi  $^{57}\text{Co}$  in Rh with this specific activity and sufficiently narrow source line width ( $\leq 0.16\,\text{mm}\,\text{s}^{-1}$ ) were supplied by the Russian Space Research Institute IKI for testing. With a rhodium matrix, no additional broadening will result from low temperatures on Mars.

Very important is an effective shielding of the detector system from direct and cascade radiation from the  $^{57}$ Co source. A graded shield consisting of concentric tubes of brass, uranium, tungsten and another outer brass cylinder has been chosen. The thicknesses and the shape of different parts of the shielding have to be optimized so that no 122 keV radiation will be seen in the detectors. This shielding also acts as collimator, limiting the maximum emission angle to  $25^{\circ}$  and reducing the cosine smearing (Klingelhöfer *et al.*, 1992b) to a level that still allows a reasonable separation of the outer lines of  $\gamma$ - and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

#### Drive system

The simplest way to meet the space and weight constraints was to scale down drive systems we have built for laboratory instruments for many years at Darmstadt (Kankeleit, 1964, 1975). We constructed a drive system which had about one fifth the size of our standard system. It has a diameter of 22 mm, a length of 40 mm and about 50 g mass (Teucher, 1994).

The system is equipped with SmCo permanent magnets and was recently optimized with regard to a homogeneous and high magnetic field in the coil gap. For this, an elaborate computer code (at the Gesellschaft für Schwerionenforschung (GSI), Darmstadt) was used and good agreement between calculations and experimental results, using a Hall sensor, was found.

The key improvements in the drive, made over the last decades, are a rigid tube connection between the driving and the velocity pick up coils in the double-loudspeaker arrangement and good shielding between the two coils to avoid crosstalk. The short tube guarantees a fast transfer

of information with the velocity of sound in the aluminium and thus a minimum phase lag and a high feedback gain margin. Fortunately, despite the increase of unwanted crosstalk due to the smaller distance between the coils, the relative contribution is still less than 0.01% in the frequency domain of the triangular waveform and is thus tolerable.

The drive operates at about 25 Hz frequency, which is also its main resonance. This low frequency allows a broad bandwidth for the closed loop system, and good performance with a triangular reference signal, but requires rather soft springs. Consequencely rotation of the drive from the horizontal to the vertical position in Earth gravity leads to a shift of about 0.4 mm in the equilibrium position of the tube. The resulting nonlinearity between velocity and pickup voltage is still tolerable within 0.1% accuracy. This can be compensated by a d.c. current if necessary. However, no correction is needed for a mission to Mars where the gravity forces are smaller by a factor of 3.

The design provides limiters to avoid destruction of the soft Kapton springs during the large accelerations associated with launch and landing. Vibration and shock tests of the drive system and the analogue part of the detector system, with shocks up to 100 g have been performed at CNES/CNRS in Toulouse, France. No problems or damage of these parts occurred.

#### Detector system and electronics

Mössbauer spectroscopy can be performed in either transmission or backscatter geometry. In transmission geometry, a well-prepared sample (relatively thin and homogeneous) is needed to avoid thickness effects (Margulies and Ehrman, 1961). Backscattering geometry does not need special sample preparation for the measurement itself, and is therefore the geometry of choice for a spacecraft mission (Galazkha-Friedman and Juchniewicz, 1989). The main disadvantage of backscattering is the secondary radiation caused by primary 122 keV radiation. For a reduction of the background at the 14.4 keV  $\gamma$ -ray and the 6.4 keV X-ray line, good energy resolution of the detector system is required. In addition a detector system covering a large solid angle and strong <sup>57</sup>Co sources are needed to minimize data acquisition time. Good resolution is even more important for elemental analysis with the X-ray fluorescence technique. For this reason, Si-PINdiodes were selected as detectors (Weinheimer et al., 1992; Held, 1993; Held et al., 1993) instead of a set of gascounters as considered by other authors (Prilutskii, 1990; Agresti et al., 1992).

We have chosen Si-PIN-diodes with  $5 \times 5 \,\mathrm{mm^2}$  or  $10 \times 10 \,\mathrm{mm^2}$  active area. A thickness of about  $400 \,\mu\mathrm{m}$  is a good choice according to our experience. The efficiencies for 6.4 and 14.4 keV radiation are nearly 100% and about 65%, respectively (Held, 1993). The energy resolution of the Si-PIN-diodes improves at lower temperature (Held, 1993; Held *et al.*, 1993). In Fig. 1 the temperature dependence of the resolution and the leakage current is depicted for two different detector sizes. The leakage current is the

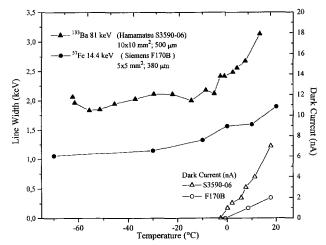
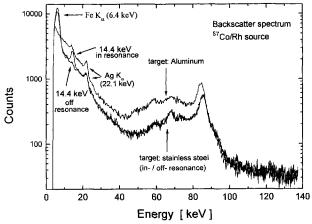


Fig. 1. Energy resolution and dark current of  $10 \times 10 \text{ mm}^2$  and  $5 \times 5 \text{ mm}^2$  PIN diodes, measured as a function of temperature (direct illumination of the detectors by the source)

dominant source for line broadening at higher temperatures. The improved resolution of the smaller diode originates from its lower capacitance. The 100 V d.c. voltage for the diodes is generated by a high frequency cascade circuitry with a power consumption of less than 5 mW. Noise contributions have to be minimized by incorporating the preamplifier–amplifier–SCA system for each detector.

Spectra of <sup>57</sup>Co/Rh radiation backscattered from an aluminium (Al) and a stainless steel (SS) plate (same recording times) are shown in Fig. 2. A continuum is seen above 122 keV resulting from the few 692 keV γ-quanta which are not completely absorbed in the shielding. Although no photo peak appears at 122 keV, this radiation shows up as a broad Compton distribution being more intense for the lower Z aluminium. A second Compton distribution originates in the detector itself as seen in the rising slope starting below 40 keV. On top of these we see a peak at 22.1 keV resulting from the silver (Ag) backing of the detector. Below this energy the 14.4 keV Mössbauer resonance line and also the 6.4 keV X-ray line



**Fig. 2.** Energy spectra of backscattered  $^{57}$ Co/Rh radiation, measured with a  $5 \times 5 \text{ mm}^2$  Si-PIN-diode, thickness  $380 \, \mu\text{m}$ , using a prototype of the MIMOS I spectrometer. Scatterers: 1 cm thick aluminium and stainless steel plates; for the case of stainless steel scattered spectra were measured in and off resonance. The recording time was the same for all three spectra

dominate in SS at zero velocity, in contrast to Al where only the (14.4–0.4) keV Compton scattered line appears.

In addition to Mössbauer spectroscopy it would be desirable to perform X-ray fluorescence (XRF) measurements for an elemental analysis of the same sample. As seen in Fig. 1, the energy resolution of Si-PIN-diodes is rather good, in particular at lower temperature (as for instance during the cold Martian night), which makes XRF feasible especially for higher Z elements. A Si-PIN detector system with an energy resolution of about 280 eV at  $-30^{\circ}$ C and  $7 \text{ mm}^2$  area was recently developed (AMPTEK, 1994). It has been shown that Charge Coupled Devices (CCD) have an excellent energy resolution if operated in a special mode (McCarthy and Wells, 1992). One of these new technological developments might be implemented in a space qualified Mössbauer instrument.

For velocity calibration a separate channel should be added, maybe with simplified electronics. The calibration spectrum for a reference sample could be recorded simultaneously with the backscatter spectra using a second source at the other end of the moving tube. A combination of reference absorbers is considered, as for instance  $\alpha$ -Fe,  $\gamma$ - or  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, both magnetically split, and the quadrupole split SNP (Na<sub>2</sub>[Fe(CN)<sub>5</sub>NO]<sub>2</sub>H<sub>2</sub>O). From the temperature dependence of the hyperfine interaction an average temperature may be deduced.

The operational control of the experiment and the data handling is done by a microprocessor which is suitable for the special applications.

# A Mössbauer spectrometer for the exploration of Mars

General remarks. The planet Mars has about half the diameter, 1/10 of the mass of the Earth, and a mean density of about 70% of the terrestrial density. The mean surface gravity on Mars is about 3.7 m s<sup>-2</sup>, approximately 1/3 of the surface gravity on Earth. The atmosphere of Mars consists mainly of CO<sub>2</sub> (95.32%), N<sub>2</sub> (2.7%), and Ar (1.6%) (Carr, 1981). The total pressure on the surface is in the range of 5–10 mbar. The temperature on Mars typically varies between about 160 and 280 K, but, depending on the latitude, somewhat higher or lower temperatures are possible (e.g. Kieffer et al., 1992). These are the main environmental constraints for the design of instruments to be deployed on the Martian surface.

Mission concepts and instrument design. There are different kinds of lander missions proposed for the exploration of the red planet. First, stationary instrument packages, as for instance the so-called small stations in the Russian Mars-94 mission, are deployed on the surface in such a way that they will form a network necessary for seismological investigations. There are plans of ESA and NASA to implement such a network by the InterMarsNet mission. Russia is intending to deploy at least two stationary landers in 1996 (Mars-94). The next step is landing a roving system which will allow investigations of many samples over a region of a few kilometres. Besides the big Russian rover Marsokhod, some small and moving

instrument carriers (rovers) have been developed which can be deployed by small landers. These include the Rocky IV rover from the Jet Propulsion Laboratory (JPL), which is part of the payload for the American Mars Pathfinder mission, and the Instrument Deployment Device (IDD) which is being developed for the ESA MarsNet proposed mission and carries the APX and Mössbauer instruments. A further miniaturized version of the IDD, called "Nanokhod", is now under development by the Max-Planck-Institute for Cosmochemistry, Mainz, in cooperation with our team at the Institute for Nuclear Physics, TH Darmstadt (see Fig. 3 and Klingelhöfer *et al.* (1995)) for the InterMarsNet mission. The Nanokhod will carry an α-proton backscattering spectrometer to determine the chemical composition of the surface, a Mössbauer spectrometer to determine the mineralogical composition of Fe-bearing phases, a small CCD camera with a resolution of about 50 μm and an X-ray fluorescence detector. A total volume of about 160 cm<sup>3</sup> is available for the Mössbauer system together with an X-ray fluorescence detector. For construction of instruments installed on the Nanokhod, advanced technologies such as hybridization, SMD (surface mounted devices), and ASICs (user defined integrated circuits) have to be used.

MIniaturized MOssbauer backscattering Spectrometer MIMOS II. By redesigning the instrument MIMOS I for the large rover (Klingelhöfer et al., 1995), we have been able to construct a further miniaturized Mössbauer spectrometer, with power consumption of about 300 mW and a mass in the order of 300 g (see preliminary design scheme in Fig. 4) which fits into the Nanokhod (see above). It can be used also as a single instrument which could be integrated for instance in a robotic arm deploying instruments on the surface. This spectrometer is of course less capable than the design for the rover (Marsokhod; see above). The main changes with respect to the large rover instrument are the use of a different microprocessor, which needs significantly less power. Instead of ADCs only discriminators will be used in each detector channel. Only energy spectra with limited resolution can be measured. The number of detector channels will range from 2 to 6, depending on the mission design. Additionally the design of the Mössbauer drive and its corresponding electronics have been changed significantly to reduce the power consumption of this part by about a factor of 10 (from about 300 mW to about 30 mW).

The general setup of MIMOS II is shown in Fig. 4. As for the instrument MIMOS I, which has been developed for the Mars-96 Russian rover mission and is described elsewhere (Klingelhöfer et al., 1992a, 1995), the drive and Mössbauer source are mounted in the centre of the instrument. The detector system consists of several detector channels each of them having a Si-PIN-diode with  $5 \times 5 \,\mathrm{mm^2}$  or  $10 \times 10 \,\mathrm{mm^2}$  of active area and a preamplifier and linear amplifier, for X-ray and  $\gamma$ -ray detection. Because of the modular design the number of detector channels can vary between 2 and about 6. This permits different constraints in power, mass and volume available for the different types of missions. Because of the dusty atmosphere, the Mössbauer system has to be dust tight and precautions have to be taken into account to avoid a dust covered entrance window.

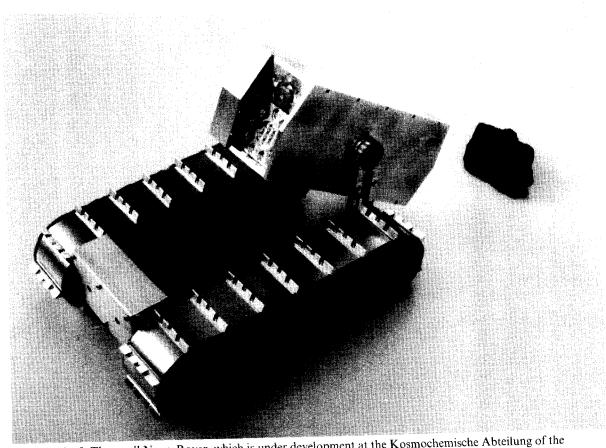


Fig. 3. The small Nano-Rover, which is under development at the Kosmochemische Abteilung of the MPI f. Chemie, Mainz. The dimensions of the Nanokhod are about  $20 \, \mathrm{cm} \times 15 \, \mathrm{cm} \times 5 \, \mathrm{cm}$ . The central box which is carrying the instruments, can be moved and rotated independently from the outer two boxes with the tracks. With courtesy Professor H. Wänke and Dr R. Rieder

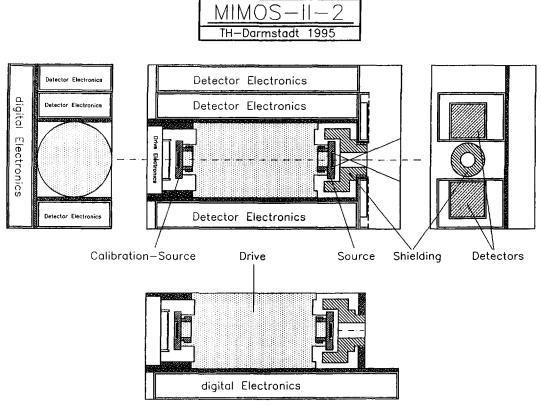


Fig. 4. Design of the Mössbauer instrument MIMOS II-2 (two detector channels) for landers and the Nanokhod, based on the design parameters described in the paper. The instrument housing has a volume of about  $220 \,\mathrm{cm}^3$  ( $4 \times 6 \times 9 \,\mathrm{cm}^3$ )

The different possible designs of a Mössbauer instrument for different missions to Mars, covering a wide range of different experimental and technical constraints, clearly demonstrate that our Mössbauer system is very flexible in its design. In some cases a reduction of capabilities is necessary to fulfil the requirements, but up to now for every mission in discussion an optimal and working compromise has been found.

#### Instrument test measurements on Mars analogues

Test measurements have been performed on two Martian analogue samples (a palagonite and an impactite) using a prototype setup of the backscatter instrument. These measurements demonstrate that the prototype is capable of acquiring Mössbauer data having a quality comparable to that obtainable from research-grade instruments.

#### Palagonite from Hawaii (PN-9)

The iron mineralogy of Martian bright regions (weathered Martian surfacial material) has been investigated by studying the mineralogy of both synthetic (e.g. Morris et al., 1989a; Morris and Lauer, 1990) and naturally-occurring spectral analogues (Allen et al., 1981; Bell et al., 1993; Berkley and Drake, 1981; Evans and Adams, 1979, 1980; Golden et al., 1993; Morris et al., 1990, 1993; Singer, 1982). Samples of palagonitic tephra collected

from the same location on the Puu Nene cinder cone, Hawaii, are among the best spectral analogues and have been studied in detail (Hawaii-34, Evans and Adams (1979, 1980); VOLO2A, Singer (1982); PN-9, Morris et al. (1993)). As represented by sample PN-9 (Morris et al., 1993), the mineralogy of iron bearing phases in increasing order of abundance is hematite, titanomagnetite, olivine, glass, pyroxene, and nanophase ferric oxide (see Table 1). Over 60% of the total iron is present as nanophase ferric oxide particles. Selective chemical extraction procedures show that these particles are the dominant pigmentary phase.

In Fig. 5 we compare the backscatter Mössbauer spectrum of PN-9 to the transmission spectrum both taken for the <1 mm sieve fraction. Transmission data for this sample have been published by Morris *et al.* (1993). Results of the analysis of the data are given in Table 1 and show that equivalent mineralogical information is obtained independent of measurement geometry.

#### Impactite-rock from Chile

Backscatter experiments have been performed on a rock sample collected from a crater near Antafagosta, Chile, South America. This crater was formed by an iron–nickel meteorite impact a few thousand years ago. The rock sample has a rough surface, similar to the Martian rocks seen on the pictures taken by the Viking landers in 1976. The backscatter spectrum given in Fig. 6 is dominated

Table 1. Comparison of transmission and backscatter Mössbauer parameters for palagonite PN-9

Backscatter mode								
Component	IS $(mm s^{-1})$	$QS (mm s^{-1})$	$B(hf) (mm s^{-1})$	B(hf)(T)	Rel. area (%)			
Np ferric oxide	+0.36	0.73			57.0 (±3.0)			
Olivine	+1.13	2.96	_	_	$13.5 (\pm 1.0)$			
Pyroxene/glass	+1.04	2.35			$4.1 (\pm 1.8)$			
Hematite	+0.38	-0.22	16.3	50.7	$5.5 (\pm 2.5)$			
Magnetite (B-site)	+0.62		14.6	45.2	$7.3 (\pm 2.0)$			
Magnetite (A-site)	+0.24	_	15.5	48.1	$2.5 (\pm 1.5)$			
Ti-magnetite	+0.73	1.2	_		$2.5 (\pm 1.5)$			
		Transmission	mode					
Np ferric oxide	+0.38	0.72	_	_	$62.5 (\pm 2.0)$			
Olivine	+1.13	2.95	_	_	$10.1 (\pm 0.8)$			
Pyroxene/glass	+1.04	2.35			$10.8 (\pm 0.8)$			
Hematite	+0.38	-0.17	16.3	50.6	$2.3 (\pm 1.0)$			
Magnetite (B-site)	+0.63		14.2	44.2	$7.3 (\pm 1.5)$			
Magnetite (A-site)	+0.24	_	15.4	47.9	$2.5 (\pm 1.5)$			
Ti-magnetite	+0.79	1.2			$4.6 (\pm 1.0)$			

Results of data analysis of the backscatter and transmission Mössbauer spectra of PN-9, a palagonite from Hawaii, both taken for a <1 mm sieve fraction. The analysis shows that equivalent mineralogical information is obtained independent of measurement geometry. The spectra are dominated by a nanophase (Np) ferric oxide component. Furthermore in increasing order of abundance hematite, titanomagnetite, olivine, glass, and pyroxene have been identified. Isomer shift (IS) is given relative to  $\alpha$ -Fe; QS, quadrupole splitting; B(hf), magnetic hyperfine field; Rel. area, area of the Mössbauer component relative to the total area of the spectrum.

by an Fe<sup>3+</sup> component (about 40% of all Fe-containing minerals), pyroxene (about 34%) and olivine (about 19%). Data analysis also indicates the presence of magnetite (about 6%) and hematite (about 1%). The uncertainties of these values are in the order of  $\pm$  3% (absolute). These results are in agreement with measurements in transmission geometry, performed on selected pieces of the rock (Knudsen, 1995).

# Laboratory weathering study of a basalt

For calibration and optimization of the backscatter instruments and for analysis and interpretation of FeMS data returned from Mars, laboratory weathering studies on Fe-bearing phases are important. We have completed initial studies of a tholeitic basalt from the Ortenberg region of Germany, which we artificially weathered in the laboratory by heating at elevated temperatures in CO<sub>2</sub> and CO<sub>2</sub>–O<sub>2</sub> gas atmospheres.

Here we discuss our preliminary studies of basalt oxidation in CO<sub>2</sub>, CO<sub>2</sub>–O<sub>2</sub> gas mixtures as a function of temperature. The experiments were done by isothermally heating polished basalt slabs in CO<sub>2</sub> and CO<sub>2</sub>–O<sub>2</sub> mixtures nominally containing 100 parts per million by volume (ppmv) of O<sub>2</sub>. Prior to heating the basalt was characterized by Mössbauer spectroscopy and electron microprobe analyses. After heating the basalt was again analysed by these two techniques.

FeMS measurements were done in transmission geometry by using a standard laboratory setup. Data were taken at room temperature using a Si-PIN detector (Fegley *et al.*, 1995b; Klingelhöfer *et al.*, 1995) and a <sup>57</sup>Co/Rh

Mössbauer source with an activity of about 90 mCi. The typical absorber thickness used for the measurements was about 25 mg cm<sup>-2</sup> and thickness effects can be assumed to be small.

Basalt is an important component on the surfaces of the terrestrial planets and the Earth's moon. The chemical weathering of basalt and of its constituent minerals (mainly pyroxene, olivine and plagioclase with minor amounts of Fe-bearing oxides) and basaltic glass is therefore probably one of the most important processes determining the chemical and mineralogical composition of the surface of Mars.

As mentioned above, the atmosphere of Mars is dominated by  $\mathrm{CO}_2$  with smaller amounts ( $\sim 0.1\%$ ) of CO and  $\mathrm{O}_2$ . Thus, one might reasonably expect that  $\mathrm{Fe^{2^+}}$ -minerals contained in basalt erupted onto the surface of Mars may be oxidized by reactions with  $\mathrm{CO}_2$  and  $\mathrm{O}_2$  in the overlying atmosphere. Schematically these reactions can be represented by the equations:

$$2\text{FeO}(\text{in basalt}) + \text{CO}_2 \rightarrow \text{Fe}_2\text{O}_3(\text{hematite}) + \text{CO}$$
 (1)

$$2\text{FeO}(\text{in basalt}) + 1/2\text{O}^{2+} \rightarrow \text{Fe}_2\text{O}_3(\text{hematite})$$
 (2)

which illustrates how chemical weathering has oxidized the surface of Mars and has also served as a sink for oxygen derived from atmospheric  $CO_2$ . This oxygen sink may be one of the major processes responsible for the loss of the oxygen originally contained in the  $\sim 1-10$  bar  $CO_2$  atmosphere needed to warm early Mars. (In this regard we note that recent work has demonstrated that only trace amounts of stratospheric  $SO_2$  in the early Martian atmosphere can prevent  $CO_2$  cloud condensation, which

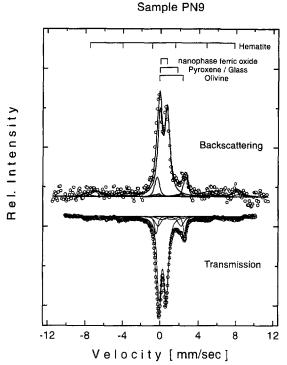


Fig. 5. Backscatter and transmission Mössbauer spectra of the sample PN-9 (<1 mm sieve fraction), a palagonite from Hawaii. The spectra are dominated by a nanophase ferric oxide component. Furthermore in decreasing order of abundance hematite, titanomagnetite, olivine, glass, and pyroxene have been identified

has been seen as a stumbling block for greenhouse warming on early Mars.)

Likewise, Fe<sup>2+</sup> oxidation schematically represented by

$$2\text{FeO}(\text{in basalt}) + \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3(\text{hematite}) + \text{H}_2(g)$$
 (3)

followed by hydrogen escape to space was probably a major sink for water on early Mars. Another important water sink was probably the formation of phyllosilicates

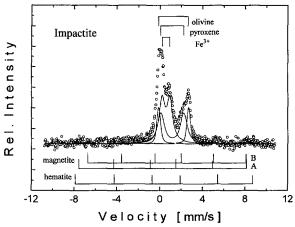


Fig. 6. Backscatter Mössbauer spectrum of an impactite from a crater nearby Antafagosta, Chile, South America. Dominant components are Fe<sup>3+</sup> (about 40% of all Fe-containing minerals), pyroxene (about 34%), and olivine (about 19%). Also indicated is the presence of magnetite (about 6%) and hematite (about 1%). Uncertainties in these values are in the order of  $\pm 3\%$  (absolute)

(e.g. Fe-bearing clays) and Fe oxyhydroxides (e.g. Lewis and Prinn, 1984).

Reactions (1)–(3) may take place either as a result of thermochemical weathering, possibly most important for recently erupted basalts and around volcanic vents, or as a result of photochemical weathering driven by the energetic solar UV light striking the Martian surface. However, at present experimental studies provide conflicting information on thermochemical and photochemical weathering reactions (Huguenin, 1973a,b; Morris and Lauer, 1980). Because of the postulated importance of reactions (1)–(3) on Mars (e.g. Lewis and Prinn, 1984), we have used Mössbauer spectroscopy to study basalt oxidation in CO<sub>2</sub>-rich gases under carefully controlled laboratory conditions.

Figure 7 shows the Mössbauer spectrum of the starting material. The Fe-bearing minerals in the basalt are clinopyroxene, olivine, and opaque oxides. The clinopyroxene contains most (about 85 wt%) of the Fe in the basalt. It is an augite containing Fe<sup>2+</sup> in the M1 and M2 crystallographic sites as well as some Fe<sup>3+</sup>. Olivine, containing 25 mol% fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) and 75 mol% forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) is the next most abundant Fe mineral and contains about 12 wt% of the Fe in the basalt, all as Fe<sup>2+</sup>. The remaining 3 wt% of the Fe is found in ilmenite (ideally FeTiO<sub>3</sub>) and titanomagnetite ( $Ti_xFe_{3-x}O_4$ ). Electron microprobe analyses show that the ilmenite in the Ortenberg basalt is actually an ilmenite-hematite solid solution, containing 5 mol% Fe<sub>2</sub>O<sub>3</sub> and that the titanomagnetite contains 25 mol% Fe<sub>3</sub>O<sub>4</sub> and 75 mol% Fe<sub>2</sub>TiO<sub>4</sub> (ulvöspinel).

As Fig. 7 illustrates, after heating for 19 days at 570°C, the Mössbauer spectrum of the basalt changed distinctly.

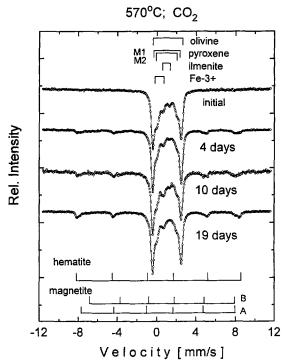


Fig. 7. Transmission Mössbauer spectra of unreacted and reacted basalt samples from the Ortenberg region in Germany. Samples were heated in CO<sub>2</sub> at 570°C for 4, 10, and 19 days, respectively

Hematite, which was almost totally absent in the unheated basalt, is now present at the level of a few percent and the magnetite abundance has also increased. Electron microprobe analyses show that the magnetite composition has changed and is depleted in Ti relative to the initial titanomagnetites. Similar results were obtained from basalts heated in the  $\rm CO_2\text{--}O_2$  gas mixtures nominally containing 100 ppmv  $\rm O_2$ . Hematite and magnetite were again produced and were present at an abundance of a few percent.

These preliminary experiments confirm the expectation (e.g. Lewis and Prinn, 1984) that Fe<sup>2+</sup> oxidation was a sink for oxygen on early Mars. The potential size of this oxygen sink can be estimated as follows. From the stoichiometry of reaction (4)

$$2FeO + O \rightarrow Fe_2O_3 \tag{4}$$

1 mol of oxygen is consumed to produce 1 mol of hematite (or maghemite). Our preliminary experiments show that a few wt% of Fe<sub>2</sub>O<sub>3</sub> were produced by basalt oxidation in the CO<sub>2</sub> and CO<sub>2</sub>-O<sub>2</sub> gas mixtures.

Because the atomic weight of oxygen is about one tenth of the molecular weight of Fe<sub>2</sub>O<sub>3</sub>, 1 mg of oxygen per gram of basalt is used up producing 1 wt% Fe<sub>2</sub>O<sub>3</sub> per gram of basalt.

These results can be applied to Mars by considering the amount of oxygen consumed in oxidizing the Martian regolith. Assuming a soil density of  $2.5\,\mathrm{g\,cm^{-3}}$  and also assuming only 1 wt% Fe<sub>2</sub>O<sub>3</sub> produced per gram of oxidized rock, we calculate that the total oxygen lost in a 1 km deep regolith is

$$(2.5 \,\mathrm{g \, cm^{-3}})(105 \,\mathrm{cm \, km^{-1}})(10^{-3} \,\mathrm{g \, g^{-1}})$$
  
= 250 g oxygen cm<sup>-2</sup>.

This is the same amount of oxygen contained in 2.8 m of water or in  $\sim 100$  mbar of CO<sub>2</sub>. Thus oxidation of Fe<sup>2-</sup> bearing minerals in basalt is potentially a potent sink for oxygen and points out the importance of Mössbauer analyses of Martian soil for constraining volatile loss from Mars.

Backscattering Mössbauer measurements on these samples using the protoflight instruments MIMOS I and II are currently in preparation for comparison with transmission data.

# Conclusion and outlook

Five years have passed since the first realistic proposals for a Mössbauer spectrometer for space applications were made (Galazkha-Friedman and Juchniewicz, 1989; Morris, 1989b). We joined the Mars-96 project about four years ago and we initially found that the method of Mössbauer spectroscopy was not well known in the planetary science community. This situation has changed significantly and Mössbauer spectroscopy is now widely accepted as a new tool for this field of science. As shown in this paper, a number of space missions have included a Mössbauer instrument in the payload.

In addition to the development of flight qualified Mössbauer spectrometers a number of laboratories including ours have started to compile multidisciplinary data on a collection of Mars analogue samples. These data include elemental composition, Mössbauer mineralogy, magnetic properties, and reflectance spectroscopy (e.g. Banin et al., 1991, 1992; Bell et al., 1990, 1993; Bishop et al., 1993a,b, 1994; Golden et al., 1993; Knudsen et al., 1990, 1992; Morris and Lauer, 1990; Morris et al., 1989a, 1990, 1993; Straub and Burns, 1991). In addition studies are performed for chemical weathering of Fe-bearing minerals believed to be present on the surface of Mars and Venus (e.g. Fegley and Treiman, 1992; Fegley and Lodders, 1993; Fegley et al., 1994, 1995a,b; Klingelhöfer et al., 1994; Straub and Burns, 1991). Such data will serve as the basis for interpretation of corresponding data returned from planetary missions.

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#### References

- Agresti, D. G., Wills, E. L., Shelfer, T. D., Iwanczyk, J. S., Dorri, N. and Morris, R. V., Development of a solid-state Mössbauer spectrometer for planetary missions. *Lunar Planet. Sci.* XXI, 5-6, 1990.
- Agresti, D. G., Morris, R. V., Wills, E. L., Shelfer, T. D., Pimperl, M. M., Shen, M., Clark, B. C. and Ramsey, B. D., Extraterrestrial Mössbauer spectrometry. Hyp. Int. 72, 285-298, 1992.
- Allen, C. C., Gooding, J. L., Jercinovic, M. and Keil, K., Altered basaltic glasses: a terrestrial analog to the soil of Mars. *Icarus* **45**, 347–369, 1981.
- AMPTEK Inc., Product information on X-ray detector with a 7 mm<sup>2</sup> Si-PIN-Diode (XR-100TR); private communication, August 1994 with Dr R. Rieder, MPI Cosmochemie, Mainz, Germany, and John Pantazis, AMPTEK Inc., Bedford, Massachusetts, U.S.A.
- Banin, A., Blake, D. F. and Benshlomo, T., Detection of nanophase lepidocrocite (γ-FeOOH) in iron-smectite Mars soil analog materials. *Lunar Planet*. Sci. 22, 49–50, 1991.
- Banin, A., Clark, B. C. and Wänke, H., Surface chemistry and mineralogy, in *Mars* (edited by H. H. Kieffer, B. M. Jakosky, C. W. Snyder and M. S. Matthew). University of Arizona Press, Tucson, 1992.
- Bell III, J. F., McCord, T. B. and Owensby, P. D., Observational evidence of crystalline iron oxides on Mars. *J. Geophys. Res.* **95**, 14447–14461, 1990.
- Bell III, J. F., Morris, R. V. and Adams, J. B., Thermally altered palagonitic tephra: a spectral and process analog to the soil and dust of Mars. J. Geophys. Res. 98, 3373–3385, 1993.
- Berkley, J. L. and Drake, M. J., Weathering on Mars: Antarctic analogue studies. *Icarus* 45, 231–249, 1981.
- Bishop, J. L., Pieters, C. M. and Burns, R. G., Reflectance spectra of sulfate and carbonate-bearing Fe<sup>3+</sup>-doped montmorillonites as Mars soil analogs. *Lunar Planet. Sci.* XXIV, 115–116, 1993a.

- Bishop, J. L., Pieters, C. M., Pratt, S. F. and Patterson, W., The effects of atmospheric pressure on infrared reflectance spectra of Martian analogs. *Lunar Planet. Sci.* XXIV, 117–118, 1993b.
- **Bishop, J. L., Peters, C. M. and Burns, R. G.,** Reflectance and Mössbauer spectroscopy of ferrihydrite-montmorillonite assemblages as Mars soil analog materials. *Geochim. Cosmochim. Acta* **57**(19), 1994.
- Burns, R. G. and Martinez, S. L., Mössbauer spectra of olivinerich achondrites: evidence for preterrestrial redox reactions. *Proc. Lunar Planet. Sci.* 21, 331–340, 1991.
- Carr, M. H., The Surface of Mars. Yale University Press, New Haven, 1981.
- Evans, D. L. and Adams, J. B., Comparison of Viking Lander multispectral images and laboratory reflectance spectra of terrestrial samples. *Proc. Lunar Planet. Sci. Conf.* 10th, pp. 1829–1834, 1979.
- Evans, D. L. and Adams, J. B., Amorphous gels as possible analogs to martian weathering products. *Proc. Lunar Planet. Sci. Conf.* 11th, pp. 757–763, 1980.
- Evlanov, E. N., Mukhin, L. M., Prilutski, O. F., Smirnov, G. V., Juchniewicz, J., Kankeleit, E., Klingelhöfer, G., Knudsen, J. M. and d'Uston, C., Mössbauer backscatter spectrometer for mineralogical analysis of the Mars surface for Mars-94 mission. Lunar Planet. Sci. XXII, 361-362, 1991.
- Evlanov, E. N., Frolov, V. A., Prilutski, O. F., Rodin, A. M., Veselova, G. V. and Klingelhöfer, G., Mössbauer spectrometer for mineralogical analysis of the Mars surface: Mössbauer source considerations. *Lunar Planet. Sci.* XXIV, 459–460, 1993.
- Fegley Jr, B. and Lodders, K., The rate of chemical weathering of pyrite on the surface of Venus. *Lunar Planet. Sci.* XXIV, 467–468, 1993.
- Fegley Jr, B. and Treiman, A. H., Chemistry of atmospheresurface interactions on Venus and Mars, in *Venus and Mars*: *Atmospheres, Ionospheres, and Solar Wind Interactions*, Geophysical Monograph 66. American Geophysical Union, 1992.
- Fegley Jr, B., Klingelhöfer, G., Brackett, R. A. and Izenberg, N., The oxidation state of the surface of Venus. *Meteoritics* 29, 465–466, 1994.
- Fegley Jr, B., Lodders, K., Treiman, A. H. and Klingelhöfer, G., The rate of pyrite decomposition on the surface of Venus. *Icarus* 115, 159–180, 1995a.
- Fegley Jr, B., Klingelhöfer, G., Brackett, R. A., Izenberg, N., Kremser, D. T. and Lodders, K., Basalt oxidation and the formation of hematite on the surface of Venus. *Icarus* 118, 373–383, 1995b.
- Fernandez-Moran, H., Hafner, S. S., Ohtsuki, M. and Virgo, D., Mössbauer effect and high-voltage electron microscopy of pyroxenes in type B samples. *Science* 167, 686, 1970.
- Galazkha-Friedman, J. and Juchniewicz, J., Martian Mössbauer spectrometer MarMös, Project Proposal, Space Research Center, Polish Academy of Sciences, February 1989.
- Gay, R., Bancroft, G. M. and Bown, M. G., Diffraction and Mössbauer studies of minerals from lunar soils and rocks. *Science* **167**, 626, 1970.
- Golden, D. C., Morris, R. V., Ming, D. W., Lauer Jr, H. V. and Yang, S. R., Mineralogy of three slightly palagonitized tephra samples from the summit of Mauna Kea, Hawaii. *J. Geophys. Res.* 98, 3401–3411, 1993.
- **Gummer, A. W.,** Effect of accumulated decay product on the Mössbauer emission spectrum. *Nucl. Instr. Meth.* **B34,** 224–227, 1988.
- Hafner, S. S., Mössbauer spectroscopy in lunar geology and mineralogy, in *Topics in Applied Physics*, Vol. 5, Mössbauer Spectroscopy (edited by U. Gonser). Springer, Berlin, 1975.
- Held, P., PIN-Photodioden als Detektoren für das Mössbauerspektrometer MIMOS zur Untersuchung der Marsoberfläche, Diploma Thesis, TH Darmstadt, Inst. f. Nuclear Physics, 1993.

- Held, P., Teucher, R., Klingelhöfer, G., Foh, J., Jäger, H. and Kankeleit, E., Mössbauer spectrometer for mineralogical analysis of the Mars surface: first temperature dependent tests of the detector and drive system. *Lunar Planet. Sci.* XXIV, 633-634, 1993.
- Herzenberg, C. L. and Riley, D. L., Mössbauer spectrometry of lunar samples. Science 167, 683, 1970.
- **Huguenin, R. L.,** Photostimulated oxidation of magnetite I. Kinetics and alteration phase identification. *J. Geophys. Res.* **78**, 8481–8493, 1973a.
- **Huguenin, R. L.,** Photostimulated oxidation of magnetite 2. Mechanism. *J. Geophys. Res.* **78,** 8495–8506. 1973b.
- Kankeleit, E., Velocity spectrometer for Mössbauer experiments. *Rev. Scient. Instrum.* **35**, 194–197, 1964.
- Kankeleit, E., Some technical developments in Mössbauer spectroscopy. *Proc. Int. Conf. on Mössbauer Spectroscopy*, Vol. 2, p. 43. Cracow, Poland, 1975.
- Kankeleit, E., Foh, J., Held, P., Klingelhöfer, G. and Teucher, R., A Mössbauer experiment on Mars. *Hyp. Int.* **90**, 107–120, 1994.
- Kieffer, H. H., Jakosky, B. M., Snyder, C. W. and Matthew, M. S., Mars. University of Arizona Press, Tucson, 1992.
- Klingelhöfer, G., Foh, J., Held, P., Jäger, H., Kankeleit, E. and Teucher, R., Mössbauer backscattering spectrometer for mineralogical analysis of the Mars surface. *Hyp. Int.* 71, 1449–1452, 1992a.
- Klingelhöfer, G., Imkeller, U., Kankeleit, E. and Stahl, B., Remarks on depth selective CEMS-backscattering measurements. Hyp. Int. 71, 1445, 1992b.
- Klingelhöfer, G., Fegley Jr, B. and Lodders, K., <sup>57</sup>Fe Mössbauer studies of the kinetics of pyrite decomposition on the surface of Venus. *Lunar Planet*. *Sci.* XXV, 707–708, 1994.
- Klingelhöfer, G., Held, P., Teucher, R., Schlichting, F., Foh, J. and Kankeleit, E., Mössbauer spectroscopy in space. *Hyp. Int.* 95, 305–339, 1995.
- Klingelhöfer, G., Fegley Jr, B., Morris, R. V., Kankeleit, E., Evlanov, E., Priloutskii, O., Knudsen, J. M. and Madsen, M. B., Mineralogy of the Martian surface analysed in-situ by Mössbauer spectroscopy, and implications for volatile evolution on Mars, Workshop on Evolution of Martian Volatiles, Lunar and Planetary Institute, Houston, Texas, February 1996.
- **Knudsen, J. M.,** Mössbauer spectroscopy of <sup>57</sup>Fe and the evolution of the solar system. *Hyp. Int.* **47**, 3, 1989.
- Knudsen, J. M., Private communication, University of Copenhagen, Denmark, 1995.
- Knudsen, J. M., Morup, S. and Galazkha-Friedman, J., Mössbauer spectroscopy and the iron on Mars. Hyp. Int. 57, 2231, 1990.
- Knudsen, J. M., Madsen, M. B., Olsen, M., Vistisen, L., Koch,
  C. B., Morup, S., Kankeleit, E., Klingelhöfer, G., Evlanov, E.
  N., Khromov, V. N., Mukhin, L. M., Prilutskii, O. F., Zubkov,
  B., Smirnov, G. V. and Juchniewicz, J., Mössbauer spectroscopy on the surface of the planet Mars. Why? Hyp. Int.
  68, 83-94, 1992.
- Lewis, J. S. and Prinn, R. G., Planets and their Atmospheres. Academic Press, New York, 1984.
- McCarthy, K. J. and Wells, A., Measurements and simulations of X-ray quantum efficiency and energy resolution of large area CCDs between 0.3 and 10 keV, *Proc. SPIE Tech. Symp.*, San Diego, California, July 1992.
- Madsen, M. B., Mørup, S., Costa, T. V. V., Knudsen, J. M. and Olsen, M., Superparamagnetism in primitive meteorites. Hyp. Int. 41, 827–830, 1988.
- Madsen, M. B., Knudsen, J. M., Vistisen, L. and Jensen, H. G., Are Phobos and Deimos carbonaceous chondrites? Mössbauer spectroscopy on carbonaceous chondrites and their relation to the Martian moons, in *The Environmental Model of Mars* (edited by K. Szegö), COSPAR Colloquia 2, January 1990.

- Madsen, M. B., Olsen, M., Knudsen, J. M., Petersen, D. and Vistisen, L., The ferrimagnetic phase in nakhla and zagami implications for the Martian fines. *Lunar Planet. Sci.* XXIII, 825–826, 1992.
- Margulies, S. and Ehrman, J. R., Transmission and line broadening of resonance radiation incident on a resonance absorber. *Nucl. Instr. Meth.* 12, 131, 1961.
- Morris, R. V. and Lauer Jr, H. V., The case against photostimulated oxidation of magnetite. *Geophys. Res. Lett.* 7, 605–608, 1980.
- Morris, R. V. and Lauer Jr, H. V., Matrix effects for reflectivity spectra of dispersed nanophase (superparamagnetic) hematite with application to Martian spectral data. *J. Geophys. Res.* **95**, 5101–5109, 1990.
- Morris, R. V., Lauer Jr, H. V., Lawson, C. A., Gibson Jr, E. K., Nace, G. A. and Stewart, C., Spectral and other physicochemical properties of submicron powders of hematite (α-Fe<sub>2</sub>O<sub>3</sub>), maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>), goethite (α-FeOOH), and lepidocrocite (γ-FeOOH). J. Geophys. Res. 90, 3126–3144, 1985.
- Morris, R. V., Agresti, D. G., Lauer Jr, H. V., Newcomb, J. A., Shelfer, T. D. and Murali, A. V., Evidence for pigmentary hematite on Mars based on optical, magnetic and Mössbauer studies of superparamagnetic (nanocrystalline) hematite. *J. Geophys. Res.* 94, 2760–2778, 1989a.
- Morris, R. V., Agresti, D. G., Shelfer, T. D. and Wdowiak, T. J., Mössbauer backscatter spectrometer: a new approach for mineralogical analysis on planetary surfaces. *Lunar Planet*. Sci. XX, 721–722, 1989b.
- Morris, R. V., Gooding, J. J., Lauer Jr, H. V. and Singer, R. B., Origins of Marslike spectral and magnetic properties of a Hawaiian palagonitic soil. *J. Geophys. Res.* 95, 14427–14434, 1990.
- Morris, R. V., Golden, D. C., Bell III, J. F., Lauer Jr, H. V. and Adams, J. B., Pigmenting agents in Martian soils: inferences

- from spectral, Mössbauer, and magnetic properties of nanophase and other iron oxides in Hawaiian palagonitic soil PN-9. *Geochim. Cosmochim. Acta* **57**, 4597–4609, 1993.
- Muir Jr, A. H., Housley, R. M., Grant, R. W., Abdel-Gawad, M. and Blander, M., Mössbauer spectroscopy of moon samples. *Science* 167, 688, 1970.
- Prilutskii, O., Space Research Institute (IKI), Moscow, Internal Report from Minsk, 1990.
- Shelfer, T. D., Pimperl, M. M., Agresti, D. G., Wills, E. L. and Morris, R. V., Backscatter Mössbauer spectrometer (BaMS) for planetary applications: transducer design considerations. *Lunar Planet. Sci.* XXII, 1229–1230, 1991.
- Shelfer, T. D., Morris, R. V., Nguyen, T. Q., Agresti, D. G. and Wills, E. L., Backscatter Mössbauer spectrometer (BaMS) for solid-surface extraterrestrial mineralogical analysis. *Lunar Planet. Sci.* XXVI, 1279–1280, 1995.
- Singer, R. B., Spectral evidence for the mineralogy of highalbedo soils and dust on Mars. J. Geophys. Res. 87, 10159– 10168, 1982.
- Solberg, T. C. and Burns, R. G., Iron Mössbauer spectral study of weathered Antarctic and SNC meteorites. *Proc. Lunar Planet. Sci. Conf.* 19, 313–322, 1989.
- Straub, D. W. and Burns, R. G., Spectral signatures of oxidized pyroxenes: implications to remote sensing of terrestrial planets. *J. Geophys. Res.* **96**(E3), 18819–18830, 1991.
- Teucher, R., Miniaturisierter Mössbauerantrieb, Diploma Thesis, TH Darmstadt, Inst. f. Nuclear Physics, 1994.
- Wdowiak, T. J. and Agresti, D. G., Presence of a superparamagnetic component in the Orgueil meteorite. *Nature* 311, 140-142, 1984.
- Weinheimer, Ch., Schrader, M., Bonn, J., Loeken, Th. and Backe, H., Measurement of energy resolution and dead layer thickness of LN2-cooled PIN photodiodes. *Nucl. Instr. Meth.* A311, 273–279, 1992.