Mössbauer spectroscopy in space

G. Klingelhöfer, P. Held, R. Teucher, F. Schlichting, J. Foh and E. Kankeleit

Institut für Kernphysik, TH-Darmstadt, 64298 Darmstadt, Germany

Nearly 40 years after the discovery of the Mössbauer effect for the first time a Mössbauer spectrometer will leave our planet to explore in situ the surface of another solar system body: the red planet Mars [1]. We are currently developing a miniaturized Mössbauer spectrometer (MIMOS) which is part of the scientific payload of the Russian Mars96 mission, to be launched within the next 2–4 years [2,3]. To fulfill the requirements for a space mission to the planet Mars, all parts of the spectrometer had to be extremely miniaturized and ruggedized to with-stand the space flight and Mars environmental conditions. The relevant parts (e.g. drive, detector system, electronics etc.) will be described in more detail and its characteristics compared to standard systems. Because of this new development there now is a growing interest to include a Mössbauer (MB) instrument in future space missions to other solar system bodies as for instance Venus, the terrestrial Moon, and a comet nucleus. Because of extremely different environmental conditions (e.g. nearly zero gravity on the surface of a comet nucleus, high pressure and temperature on the surface of Venus, etc.) different instrument designs and concepts are required for different missions. We will present some ideas for various types of missions, as well as the motivation for using Mössbauer spectroscopy in these cases.

1. Introduction

The primary goal of planetary exploration is to achieve a deep understanding of the Solar System. To understand the origins of the Solar System and the origin of life itself is one of the longest standing goals of human thought. Today it is generally accepted, that our Sun and its planets have formed out of an interstellar cloud which collapsed due to gravitational forces, forming a disk shaped so-called protosolar nebula, with the young star in the center. The interstellar cloud formed out of the interstellar medium which consists of remnants from nova and supernova explosions. Besides silicates and carbon grains also metal grains, oxides and sulfides should have been present. One of the important elements present in the protosolar nebula with relatively high abundance is iron. Furthermore, it is believed that simple molecules such as water (H₂O), carbon monoxide (CO) and hydrocarbons (combinations including hydrogen and carbon) were formed in this protosolar nebula [4].

Such disk shaped and dust grain containing protosolar nebulae have now been observed. One of them is surrounding the young star Beta pictoris [5,6].

As we know very well, at least in one case – our own Solar System – a variety of different objects were formed: planets, meteoroites, asteroids, and comets. At least on one of these planets, the Earth, life has formed. The different types of bodies in our Solar System can be classified as indicated in fig. 1. The Sun and the planets are processed bodies, whereas asteroids are supposed to be only partially processed. The comets are believed to be remnants of the protosolar nebula.

The primary goals of the exploration of our Solar System, as identified by the Solar System Exploration Committee (SSEC), an ad hoc committee of the NASA Advisory Council, established in 1980, are the following:

- determination of the origin, evolution and present state of the Solar System;

- understanding of the relationship between the chemical and physical evolution of the Solar System and the appearance of life;

- understanding of the Earth through comparative planetary studies;

- survey of resources available in near-Earth space.

The process of birth and evolution of our Solar System can be investigated indirectly by studying all the different members of the planetary system, which in some respect represent different stages in the evolution of the solar system, by means of remote sensing and planetary robotic space missions. One of the key elements in the evolution of the Solar System is iron. The chemistry of iron is strongly coupled to



Fig. 1. Schematic history of circumstellar dust grains from their birth in stellar atmospheres to their analysis in terrestrial laboratories. With courtesy of ESA [83].

the chemistry of abundant elements as hydrogen, oxygen and carbon. By studying the cosmic history of iron we have the possibility of understanding the chemical evolution of matter and life itself. For instance, the study of the oxidation state of iron in the surface rocks of the planets is an important aspect because according to theoretical studies iron contained in a planetary body should be the more oxidized the farther away from the sun this body has formed. Here Mössbauer spectroscopy is the obvious tool, because it is a unique method for determining the oxidation state of the element iron. Furthermore, the mineralogical composition of iron containing surface rocks and their weathering products can be determined directly. This will contribute to an understanding of the history and development of the planetary surface as, for instance, the Martian surface. On Mars there is evidence that in the past liquid water may have been present on the surface which might have led to the formation of life similar to the Earth.

Mössbauer spectroscopy has made decisive contributions to the understanding of the evolution of the Solar System by laboratory studies of meteorites, especially carbonaceous chondrites (see for instance refs. [7,8]), which are available on Earth, and laboratory studies of Lunar material (see for instance [9-12]), which has been brought back to Earth by the American Apollo missions and the Soviet robotic sample return missions. But up to now no in situ measurements have been performed by Mössbauer spectroscopy as part of planetary missions, because no space qualified instrument has been available. This situation has changed within the last 2 to 3 years. For the Russian Mars96 mission a Mössbauer spectrometer was proposed [13] and has finally been included in the scientific payload. We are currently developing this instrument at the Technische Hochschule (TH) Darmstadt [2,3,14,15]. A similar instrument is currently under development in the USA [16-18]. These developments have created a lot of interest in Mössbauer spectroscopy among planetary scientists, and today for several other missions the use of a Mössbauer spectrometer is under discussion, as for instance different kinds of Mars missions, as well as missions to the planet Venus, the Moon and a comet. In the following chapters we will discuss in more detail the technical design of a space qualified Mössbauer spectrometer and the instrument which will be installed on the Russian Mars Rover for the Mars96 mission. Other missions require different designs due to different technical constraints (as for instance limited power resources) or due to different environmental conditions (high temperature on the surface of Venus). We will present some different designs for such missions as well as the motivation for including a Mössbauer instrument in missions to targets others than the planet Mars.

2. General design of a space qualified Mössbauer spectrometer

Planetary and interplanetary space missions usually have limited resources in mass, volume and electrical power, especially if the instruments should be deployed on the surface of a solar system body. Due to these constraints for a space qualified

Mössbauer spectrometer the standard laboratory equipment had to be extremely miniaturized and optimized in power consumption. All the different 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 the Mössbauer system has to boot with a simple "on" command and/or by switching on the power. In all cases which will be discussed in this paper the measuring time for a particular sample has to be in the order of 1-10 h. Therefore, high detection efficiency is extremely important.

There also should be a possibility to calibrate the instrument in situ during the measurements, or maybe before and/or afterwards. One possible solution for this would be to have a second, less intense radioactive source mounted on top of the drive and a reference absorber in transmission geometry.

The main parts of the Mössbauer (MB) spectrometer are the electromechanical vibrator, usually mounted in the center of the instrument, the detector system, the electronics for the detector and the vibrator, the ⁵⁷Co MB source, a multilayered radiation shield, and a γ - and X-ray window. The general design of these components suitable for space applications will be described in the following.

2.1. MÖSSBAUER SOURCE AND SHIELDING

The highest possible source strength is desirable; however, the size of the source has to fit in the given system. On the other hand, the size of the source is dictated by the specific activity, which is limited by the requirement that over a certain period (some years) the source line width should not increase significantly (in the order of a factor of 2–3). Calculations indicate an optimum at 1 Ci/cm^2 [19–21]. Sources of 150–300 mCi ⁵⁷Co in Rh with this specific activity and of comparable quality to commercial sources were supplied by the Russian Space Research Institute IKI for testing. With a rhodium matrix no additional broadening due to the low temperatures should occur.

Most important is an effective shielding of the detector system from direct and cascade radiation. A graded shield consisting of concentric tubes of brass, U, W and another outer brass cylinder has been chosen. The thickness 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 (see also section 3.1).

This shielding also acts as a collimator, limiting the maximum emission angle to 25° and reducing the cosine smearing [22] to a level that still allows a reasonable separation of the outer lines of γ - and α -Fe₂O₃.

2.2. DRIVE SYSTEM

The simplest way to fulfill the space and weight conditions was to scale down the drive systems we have been building in this institute [23,24] for many years. A decisive aspect in this scaling is the size and the mass (2-4 g) of the sources. We thus constructed a drive 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 [25].

The system equipped with SmCo permanent magnets was newly 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 decisive improvements of the drive, made in the last decades, are a rigid tube connection between the driving and the velocity pick up coils in the doubleloudspeaker 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 aluminum 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.

These relations are depicted in fig. 2 in the Bode diagram of the transfer function, which is the output voltage over input current as a function of frequency. The 1/f behavior above the main resonance at about 25 Hz extends up to 20 kHz. The small dipole at about 2 kHz is caused by a coupling of the Co source to the tube



Fig. 2. Amplitude abs(H) and phase transfer function of the drive as function of frequency of the input current. Abs(H), given in arbitrary units, is the ratio of the output voltage of the pickup coil and the input current of the driving coil. The phase is given in degrees. Also indicated is the crosstalk and the calculated transfer behavior for an Al tube (dashed line).

but is of no significant relevance for the feedback behavior. The available gain at a phase of -180° determines the possible feedback gain of 3×10^{3} , which is excellent. Because of the steep phase change at this point additional filtering makes no sense and was not used. The figure also shows the calculated transfer function for an Al tube having a speed of sound of 5000 m/s. The first resonance of the tube shows up at 1/T = c/l = 25 kHz (see fig. 2). This is in reasonable agreement with the experimental results considering the rather complex structure of the tube. Due to the shorter tube this drive achieves a feedback gain and performance in triangular velocity motion superior to our standard drive. For the light weight sources the linearity is better in comparison to the standard drive, and the difference signal is nearly free of ringing.

The drive will be running at about 25 Hz frequency at which it also has its main resonance. This low frequency allows a broad bandwidth for the closed loop system and good performance with triangular reference signal. But this requires rather soft springs. As a consequence a rotation of the drive from horizontal to vertical position in earth gravity leads to a shift of the equilibrium position of the tube of about 0.4 mm. The resulting nonlinearity between velocity and pickup voltage is still tolerable within 0.1% accuracy. In principle this can be compensated by a DC current if necessary. In case of a mission to Mars with a factor 3 smaller gravity forces this will create no problem and no correction is needed.

Concerning the large accelerations during launch and landing the construction provides limiters to avoid the destruction of the soft Kapton springs. The whole system including the drive has to survive an extremely rough testing procedure. Vibration and shock tests of the drive system and the analog 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.

2.3. DETECTOR SYSTEM AND ELECTRONICS

Mössbauer spectroscopy can be performed in transmission geometry as well as in backscattering geometry. In transmission geometry a well prepared relatively thin and homogeneous sample is needed to avoid thickness effects [26]. The backscattering geometry does not need sample preparation for the measurement itself. Therefore, if somehow possible in a space mission, a Mössbauer experiment should be performed in backscattering geometry to avoid sample preparation.

For a backscatter geometry a detector system covering a large solid angle is needed to minimize data acquisition time. Because secondary radiation created by the 122 keV γ -rays creates background in the 14.4 and 6.4 keV window good energy resolution of the detector is desirable such that a narrow window set on these lines will produce a good signal to background ratio.

We have chosen silicon-PIN-diodes [27] with $5 \times 5 \text{ mm}^2$ or $10 \times 10 \text{ mm}^2$ active area. A thickness of about 400 μ 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. Diodes with a larger thickness and therefore higher efficiency for the 14.4 keV radiation, having a smaller capacity and minimal leakage current, are not available today, but would lead to a significantly better performance of the detector system.

The energy resolution of the Si-PIN-diodes improves at lower temperatures [28]. Fig. 3 shows the energy spectra for two temperatures. In fig. 4 the temperature dependence of the resolution and the leakage current is depicted for two different detector sizes. The leakage current is the dominant source for line broadening at higher temperatures. The improved resolution of the smaller diode originates from its lower capacity.

Spectra of ⁵⁷Co/Rh radiation backscattered from an Al and a stainless steel (SS) plate, which are equal in recording time, are shown in fig. 5. A geometry as described in section 3.1 was used for these measurements. A continuum is seen above 122 keV resulting from the few 692 keV γ -quanta which are not completely absorbed in the shielding. No photo peak appears at 122 keV. But this radiation shows up in a broad Compton distribution being more intense for the lower Z Al. 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 due to the Ag backing of the detector. Below this energy the 14.4 keV MB resonance line and also the 6.4 keV X-ray line dominate in SS at zero velocity, in contrast to Al where only the 14.4–0.4 keV Compton scattered line appears.



Fig. 3. Energy spectra of a 57 Co/Rh source with a 5 \times 5 mm² PIN-diode of 380 μ m thickness at two temperatures (direct illumination of the detectors by the source).



Fig. 4. Energy resolution and dark current of a $10 \times 10 \text{ mm}^2$ and a $5 \times 5 \text{ mm}^2$ PIN diode, measured as a function of temperature (direct illumination of the detectors by the source).



Fig. 5. Energy spectra of backscattered ⁵⁷Co/Rh radiation, measured with a 5 × 5 mm² Si PIN diode, thickness 380 μm, using a prototype of the MIMOS I spectrometer. Scatterers: 1 cm thick aluminum and stainless steel (SS) plates; for the case of SS scattered spectra were measured in and off resonance. The recording time was the same for all three spectra.

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. 4 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. Recently a Si-PIN detector system has been developed with an energy resolution of about 280 eV at -30° C. The size of the PIN detector was about 7 mm² [29,74]. Another possibility is to use a different X-ray detector for XRF. This could be a small HgI₂ detector which gives the best resolution even at room temperatures [18,30]. Recently it has been shown that charge coupled devices (CCD) have an excellent energy resolution if operated in a special mode [31]. One of these new technological developments will be implemented in a space qualified MB instrument. This will allow a more accurate interpretation of the Mössbauer data.

As discussed above, a high energy resolution is required for each of the diodes. Therefore the noise contributions have to be minimized. That means each of the detectors needs its own preamplifier-amplifier-ADC (or -SCA) system (see section 3.1, figs. 7 and 8). For the measurement of the energy spectra a 12 bit ADC, selected for good differential linearity, is used. Only the most significant 8 bits are read out. Therefore no sliding scale technique is required. These measurements also allow a performance check of the system.

At least one channel should be used for high resolution X-ray fluorescence spectroscopy. This one could be most simply run under identical conditions as the other channels. For velocity calibration a separate channel should be added, possibly with simplified electronics. The 100 V DC voltage for the diodes are generated by a high frequency cascade circuitry with a power consumption of less than 5 mW.

The operational control of the experiment and the data handling is done by a microprocessor which is suitable for the special applications (fig. 8). Two possible solutions are described in the following chapters.

3. Possible targets in the Solar System

The activities leading to the development of a space qualified Mössbauer instrument were started in connection with the worldwide efforts of the exploration of Mars [2,13,15,16,32]. After it had been shown that the construction of a space qualified Mössbauer spectrometer (MBS) is possible, the discussion on the implementation of a MBS in missions to planetary bodies other than Mars began. First of all, of course, some of the actual mission plans were reanalysed in respect to the inclusion of MBS after planetary scientists recognized the new possibilities using MBS. Some of these missions for which the inclusion of a MBS is now considered seriously, will be discussed in the following chapters. There are of course some solar bodies which are currently not in the focus of solar system exploration programs, but would be of scientific interest to explore. We will discuss very briefly some aspects of scientific interest to explore these objects.

It turned out in the discussion of space application of Mössbauer spectroscopy, that a very important aspect is the laboratory work accompanying a certain space mission. For example, the work on Mars sample analogues [33–39] or the work on atmosphere-surface interaction on Venus [40–44] is extremely important for the preparation of the space experiment itself and also for the interpretation of data which will be received from the space mission. In respect to Mars and Venus a nummer of research groups have started the investigation of different possible analogue samples. The samples are investigated not only by MBS but also by other methods. Some of them are also part of these space missions.

3.1. MARS

In the coming decades the red planet Mars, the colour of which is due to iron oxides, will play an essential role in the study of the Solar System by spacecraft missions. There are plans at the space centers NASA (United States of America), ESA (Europe) and IKI (Russia) to install stationary and/or mobile systems on the surface of Mars. Part of the scientific payload of the Russian Mars96 mission [45] is a ⁵⁷Fe-Mössbauer (MB) spectrometer installed on a rover of about 1 m size to be placed on the surface of Mars [14,15].

3.1.1. Motivation, goals

The elemental composition of the Martian soil was determined by X-ray fluorescence analysis during the Viking mission in 1976 [46], but not its mineralogical composition. One suggestion is that it is composed mainly of iron-rich clay minerals, with an iron content of about 14 ± 2 wt%. The soil also contains about 5 wt% of a strongly magnetic mineral, perhaps maghemite (γ -Fe₂O₃) [46], or nanocrystalline hematite (α -Fe₂O₃) [47]. Besides other elements, about 0.6% \pm 0.2% of Ti were found by X-ray fluorescence. It will be significant to establish whether the magnetic phase on the surface of Mars contains titanium or not. The pathways of formation of maghemite and titanomaghemite are very different [1,48]. Also of extremely great interest is the oxidation state of the iron and the mineral composition of the Mars surface [49–51]. To both questions MB spectroscopy can provide important information. The question, "Why have a MB experiment on Mars?", has been extensively discussed by Knudsen [1,5,32].

One particular question is whether the SNC meteorites unequivocally can be shown to have come from Mars or not? If they really originate from the red planet, how did they get to Earth? Mössbauer spectroscopy can contribute significantly to the answer of this question by comparing the laboratory Mössbauer results with the data from the in situ analysis on Mars. If it will really be shown that the SNC's originate from Mars we already have a few kg of Martian material available for laboratory research on our planet.

3.1.2. A Mössbauer spectrometer for the exploration of Mars

General remarks. The planet Mars has about half the diameter of the Earth, about 1/10 of the mass of it, and a mean density of about 70% of the terrestrial density. The mean surface gravity g on Mars is about 3.7 m s^{-2} , approximately 1/3 of the surface gravity on Earth. The atmosphere of Mars consists mainly of CO₂ (95.32%), nitrogen N₂ (2.7%), and argon (1.6%) [49]. 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 on the surface somewhat higher or lower temperatures are possible. These are the main environmental constraints for the design of instruments to be deployed on the Martian surface, leading to general requirements which will be discussed for the case of an MBS in the following section.

Requirements for the instrument. There are different kinds of missions proposed for the exploration of the red planet. First of all stationary instrument packages, as for instance the so-called "small stations" in the Russian Mars94 mission, are supposed to be 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. Russia is going to deploy at least two stationary landers in 1996 (Mars94). The next step further is the landing of a roving system which will allow to investigate more than one single sample. Besides the big Russian rover for the Mars96 mission, scheduled to launch in 1998, also some small rovers have been developed as for instance the Rocky IV from Jet Propulsion Laboratory (JPL), which is part of the payload for the American Mars Pathfinder mission, or the Instrument Deployment Device (IDD), developed for the ESA MarsNet mission proposal. A miniaturized version of the IDD is now under development for the Mars94 mission.

In the following the requirements for a Mössbauer instrument, which are valid for all the different Mars missions, will be discussed. After this the specific constraints for the different missions and their influence on the instrument design will be given.

First of all one has to have a look on the possible source activity which will be available on the Martian surface. For all missions proposed up to now a cruise duration of about 1–2 years is calculated which is equivalent to about 2–3 half lives of the Mössbauer source.

As shown above, sample preparation as needed for a transmission experiment has to be excluded. However, the MB backscattering technique is highly suitable for a rover mission with the possibility for selecting samples. This was already recognized in an early proposal for this mission [13].

The main disadvantage of backscattering is the secondary radiation caused by the 122 keV transition. For a reduction of the background at the 14.4 keV γ -ray and the 6.4 keV X-ray line, good energy resolution of the detector system is required as well as high count-rate capabilities with the strong sources to be used. Good resolution is even more important for elemental analysis with the X-ray fluorescence technique. For this reason Si-PIN-diodes were chosen as detectors instead of a set of gas-counters considered by other authors [52,53].

The general setup of our miniaturized Mössbauer backscattering spectrometer (MIMOS) is shown in fig. 7.

The detector system consists of silicon-PIN-diodes [27] with a $5 \times 5 \text{ mm}^2$ or $10 \times 10 \text{ mm}^2$ of active area in an array arrangement as indicated in two options in fig. 7. The temperatures on Mars are well below freezing point of water. Fortunately, the energy resolution improves at lower temperatures [28]. For the interpretation of the MB spectra it is important to resolve the Ti X-rays of 4.51 keV [32].

As mentioned before, a rotation of the drive from horizontal to vertical position in Earth gravity leads to a shift of the tube equilibrium position of about 0.4 mm, resulting in a nonlinearity within the 0.1% accuracy. In principle this can be compensated by a DC current if necessary. On Mars with a factor of 3 smaller gravity forces than on Earth this will create no problem and no correction is needed.

Because of the dusty atmosphere, the MB system has to be dust tight and precautions have to be taken into account to avoid a dust covered entrance window.

Velocity calibration and control of linearity will be done by simultaneously recording a calibration spectrum using a second source at the other end of the moving tube. A combination of reference absorbers is considered, as for instance α -Fe, γ - or α -Fe₂O₃, both magnetically split, and the quadrupole split SNP (Na₂[Fe(CN)₅NO]·2H₂O). From the temperature dependence of the hyperfine interaction an average temperature may be deduced.

The experiments have to withstand accelerations over a broad bandwidth in frequency up to 200 g as well as the large diurnal temperature variations on the Martian surface. The memory and microprocessor chips have to survive two years of cosmic ray irradiation.

According to the COSPAR requirements (less than 300 spores per m^2 [54]), sterilizing procedures are necessary before departure and have to be considered in the construction.

The large Russian Mars rover. The Russian Mars96, which is scheduled to launch in 1998, will deploy a balloon (French contribution) and a rover to the lower atmosphere and the Martian surface respectively. The Mössbauer instrument is part of the scientific payload of the rover. The big step forward in having a rover compared to the stationary Viking and Mars94 landers is the possibility to study different samples at different geologically attractive sites. For the MB setup it will be of importance to record spectra of the fine soil on the surface, of rocks and of the deepest few centimeters of the soil, which may be accessible by using one of the wheels of the rover for digging, or possibly a drilling device.

For the Mars96 mission, the rover of overall size of 1 m and weight of about 70 kg will supply a total of 10–15 W electric power on average. This power has to be shared between experiments and the movement devices of the rover itself.

Finally the total average power available for experiments depends on the distance the rover is decided to go. The total weight for about eight experiments will be limited to 10-15% of the weight of the rover. Considering all these facts the Mössbauer spectrometer to be implemented on the rover is limited to a total mass of less than 500 g and an average power consumption of about 3 W.

The MB experiment will be positioned together with an α -backscattering experiment [30] and a small TV camera on a robotic arm (see fig. 6), which is under development at Vinii Transmash, St. Petersburg, and the Space Research Institute (IKI), Moscow, Russia.

As mentioned above, the Martian soil contains a significant amount of a mag-





Fig. 6. Scheme of the Russian Mars rover, together with the robotic arm mounted on the chasis. The arm (2) will carry the instrument head (1) with the Mössbauer spectrometer, an α-backscattering and X-ray spectrometer, a CCD camera and some devices for sample preparation. The rover has three axes, six wheels (4) and instrument boxes (3). (a) shows the arm in the parking position, (b) shows it in working position. With courtesy of Dr. S. Linkin and Dr. Rodin, IKI.

netic material. It would be desirable to also have the possibility of magnetic separation which would allow this component to be identified with high accuracy. The use of permanent magnets as in the Viking mission [46], or maybe of a magnet array as now included in the US Pathfinder mission [55,56], in combination with the MB instrument will allow this. This proposal [57] is now seriously considered for the Mars96 mission.

Very important is the ambient temperature, which will change between about 180 and 290 K during a Martian day for equatorial landing sites. There is no power left for temperature control but these temperature fluctuations may be considered of great scientific advantage for both the detectors and the samples, which may be investigated over a range of measurable temperatures.

Another problem is microphonics due to other experiments, the rover itself, or in particular to winds or even dust storms expected in Martian autumn. This makes a sturdy connection between sample and MB drive essential. For these reasons the pickup voltage from the drive will be used as a check for the level of microphonics before the start of the MB experiment.

Due to restrictions in data transfer (20 min Mars-Earth travel time; low roverorbiter transfer rate), the MB system has to boot with a "power on" command and the data have to be stored within the system until a contact between rover and orbiter is established.

The measuring times for a particular sample have to be of the orders of a few hours depending on the rover program. Because of the expected complex spectra over a large dynamic range in velocity high detection efficiency is extremely important.

The system has the size of a soft drink can, a weight of less than 500 g and a power consumption of less than 3 W, as defined at the beginning (see above). The ⁵⁷Co source is mounted to the small drive and surrounded by a graded shield. Collimated radiation passes through a Be window and the reemitted radiation is detected by a ringlike array of PIN-diodes behind the same Be window. To achieve noise reduction and high count-rate there are six independent preamplifieramplifier-ADC channels. Data storage and data transfer are controlled by a transputer which also produces the velocity reference signal. There is a seventh channel for velocity calibration of the MB drive with a small source mounted to the top of the drive and a reference absorber in transmission geometry (see fig. 7). In addition there are temperature sensors active during the MB experiment, and during the off time vibrations will be detected.

Most important is an effective shielding of the detector system from direct and cascade radiation. The 8 mm inner diameter graded shield consists of concentric tubes of 0.5 mm thick brass, 1 mm U, 1 mm W and another 0.5 mm brass. No 122 keV radiation is seen in the detectors. This shielding acts also as collimator, limiting the maximum emission angle to 25° and reducing the cosine smearing [22] to a level that still allows a reasonable separation of the outer lines of γ - and α -Fe₂O₃.



Fig. 7. Mössbauer spectrometer MIMOS for backscattering geometry with two possible detector arrangements as seen from the bottom.

A high energy resolution is required for each of the diodes. That means each of the detector needs its own preamplifier-amplifier-ADC system (see figs. 7 and 8). A 12 bit ADC, selected for good differential linearity, is used. Only the most significant 8 bits are read out. Therefore no sliding scale technique is required. Two digital windows at 6.4 and 14.4 keV are set by the transputer software. The performance of the system has to be checked repeatedly. This is most easily done by taking energy spectra. The ADC conversion time has to be short for the rather high count-rates expected. Also for this reason the Gauss filter amplifiers provide bipolar output pulses allowing good resolution up to 10 kHz.

The operational control of the experiment and the data handling is done by a microprocessor which is suitable for fast real time applications (fig. 8). The choice of the Transputer T225 microprocessor was also biased by the broad experience we have in using them in a transputer tree for the read out of a multiwire chamber for the Kaon spectrometer at GSI [58,59].



Fig. 8. Scheme of the electronic part of MIMOS. "Amp" consists of the preamplifier, connected to the PIN diode, and the Gauss amplifier. For detailed description see text.

Main parts of the CPU module are a 16 bit transputer T225 running with 20 MHz clock frequency, 64 kByte static RAM to hold the program and spectrum data and some control logic contained in an ASIC (application specific integrated circuit). The control program is stored in a 128 KByte (E)EPROM and will be transferred to the RAM via a transputer link at power on time. The large (E)EPROM capacity allows to store more than one copy of the control program in order to increase security against bit faults. Communication with the host computer of the rover will be done using a second transputer link or some other serial interface. All parts of the CPU module are realized in low power CMOS technology.

The transputer generates a clock driving the analog reference signal for the drive using a 12 bit DAC. In the multiscaler mode it provides the digital filtering of the 6.4 and 14.4 keV ADC signals. The selected events from the different detector channels are routed by the transputer to the actual velocity channel of the corresponding Mössbauer spectra. With about 25 Hz drive frequency and 512 channels per MB spectrum all this has to be done in less than about 80 μ s.

In addition measurements of temperature, vibrations and energy spectra are controlled by the transputer.

Small stationary stations and small rovers. Besides the Mars96 mission Russia is going to launch the Mars94 mission two years earlier (in 1996). Both missions have been shifted for two years in respect to previous time schedule. In the Mars94 mission the deployment of two stationary stations is planned. A technical scheme of such a station is shown in fig. 9. These so-called small stations have originally been designed for meteorological investigations, but a number of other instruments have been added meanwhile. The payload includes a meteorological complex with sensors for pressure, temperature, humidity, wind velocity, and solar direction, an



Fig. 9. Technical scheme of the "small stations" of the Russian Mars94, without a Mössbauer instrument. The MBS would be installed on the free leaf, similar to the APX instrument. By courtesy of Barbara Brown, Jet Propulsion Laboratory (JPL), NASA.

alpha-backscattering spectrometer for chemical analysis of the surface, a magnetometer, a seismometer, and an oxidation experiment (MOx), looking for the degree of oxidation of different materials.

After shifting the time schedule for two years it was proposed to also add a Mössbauer instrument. With respect to the large Mars rover the constraints in power and mass are much more severe: the mass has to be below about 300 g, and the total average power consumption has to be less than 300 mW! This is due to the fact that the available power is limited by the RTG (radioisotopic generator) used for these stations, which produces about 200 mW continuously.

By redesigning the instrument for the large rover we have been able to construct a 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. 10). This spectrometer is of course less capable than the design for the rover (see above). The main changes with respect to the large rover instrument are the use of a different microprocessor, which needs significantly less power, but is not as capable as the T225. Furthermore, instead of ADC's in each detector channel only discriminators will be used. No energy spectra can be measured. Only two detectors



Fig. 10. Preliminary design of a possible Mössbauer instrument for the small station, based on the design parameters described in the paper. The instrument housing has a volume of about $220 \text{ cm}^3 (4 \times 6 \times 9 \text{ cm}^3)$.

will be used instead of six in the rover instrument. 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 to about 30 mW)!

This instrument will allow only the measurement of one Mössbauer spectrum using the 14.4 keV radiation. The instrument may be installed on one of the four leaves of the Russian small stations. Such an instrument could be used also for other missions where similar power restrictions apply (for instance the MarsNet program of ESA [60]). In the MarsNet proposal a Mössbauer instrument is included.

For such small stations different kinds of small, and moving instrument carriers have been developed. They got very different names. In the ESA MarsNet program a so-called instrument deployment device (IDD) was included, carrying the APX- and the Mössbauer instrument. In the American Pathfinder the American micro-rover Rocky IV is included. It will carry the APX instrument. At the moment a so-called Nano-Rover is 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. 11). This "Rover" is smaller than the IDD. The Nano-Rover 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 cm³ is available for the Mössbauer system together with an Xray fluorescence detector. For the construction of the instruments installed on this Nano-Rover advanced technologies as hybridisation, SMD, ASICs, etc. have to be used. It has been demonstrated by the Clementine mission (see section 3.3) that such new technologies, which are usually not space qualified, are working very properly in space applications. This Nano-Rover might be installed on a Russian small station supposed to fly in 1996.

It is of course not clear whether this very capable instrument package will be launched in 1996 or not. But such a sophisticated instrument package could be installed on a lot of different missions to Mars, the terrestrial Moon, asteroids and comets. There are also some terrestrial applications one might think of.

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



Fig. 11. The small Nano-Rover, which is under development at the MPI Kosmochemie, Mainz. The dimensions of the Nanokhod are about 20 cm × 15 cm × 5 cm. The central box which is carrying the instruments, can be moved and rotated independently from the outer two boxes with the tracks. By courtesy of Professor H. Wänke and Dr. R. Rieder.

some cases a reduction of capabilities is necessary to fulfil the requirements, but up to now for every mission an optimal and working compromise has been found.

3.2. VENUS

The planet Venus is the planet second nearest to our Sun. Venus is very similar to our planet Earth in size, mass and density, in contrast to the planet Mars. Nevertheless, Venus is also very different from Earth in environmental conditions as also Mars is. The planet is completely covered by clouds. The surface temperature is about 500°C and the surface pressure is about 100 bar. The atmosphere consists mainly of CO₂ (about 96.5% \pm 8%). The high temperature is interpreted as a result of the so-called green house effect. It is obvious that the evolution of the planets Venus, Earth and Mars, born at the same time, has ended up in very different states. One of the major questions is what is the reason of this? Could it be the difference in size? This might explain the difference between Earth and Mars. But this cannot hold for Venus. To solve this puzzle, which will help to understand the formation and evolution of the solar system, and to predict the future evolution of the Earth, it is necessary to explore the surface of Venus in respect to mineralogy, chemistry, morphology, as well as the surface-atmosphere interaction.

3.2.1. Motivation and goals for the exploration of Venus

In the last 20 years a number of space missions have been send to Venus. From the Russian landers (Venera 9 to 14) the chemical composition at the ground of two landing sites could be determined. Recently, the very successful American Magellan space probe mapped the complete Venus surface by radar and revealed evidence for both evolved compositions (steep-sided domes and festoons; [61]) and primitive compositions (sinuous channels and large flood basalts [62]). Also reflectivity values vary very sharply at certain altitude [63].

However, the elemental and mineralogical characteristics of this observed range of morphological and radar property variability are not presently known. Besides other open questions there is a major uncertainty about the oxidation state of the surface of Venus [64] and the interaction of the atmosphere and surface rocks [65]. From the data of the Pioneer Venus spacecraft, the Venera 11/12 spacecraft, etc., a theoretical model for the sulfur geochemical cycle on Venus has been proposed [66,67] (fig. 12). An important component of this sulfur geochemical cycle is the chemical weathering of pyrite. This was predicted to be a source of reduced sulfur gases at the surface of Venus. After the Pioneer Venus and Magellan missions pyrite was also proposed to be present in low emissivity regions in the highlands of Venus [68–70].

The questions on the oxidation state of the surface of Venus and whether pyrite is stable or not have been investigated by laboratory experiments [40-44]. A detailed experimental Mössbauer study of the kinetics and mechanism of the chem-



Fig. 12. Modified version of the Venus sulfur cycle proposed by Von Zahn et al. in 1983 and Prinn in 1985. According to the results from refs. [41,43] the reaction sequence pyrite → pyrrhotite → Fe oxide has been incorporated into this diagram.

ical weathering of pyrite (FeS₂) under Venus surface conditions showed that pyrite is unstable on the Venusian surface [43,41]. All studies performed with CO₂ and CO₂ gas mixtures (CO–CO₂, Ar–CO₂, H₂–CO₂, CO–CO₂–SO₂) along five isotherms in a temperature range of 390–531°C showed that pyrite thermally decomposes to monoclinic pyrrhotite (Fe₇S₈). By continued heating more Fe-rich hexagonal pyrrhotite is formed (see fig. 13). During this process the pyrrhotites are oxidized to form magnetite (Fe₃O₄), which is converted to maghemite (γ -Fe₂O₃) and then to hematite (α -Fe₂O₃). This reaction sequence could be determined by X-ray diffraction and Mössbauer spectroscopy (see fig. 13). The reaction rate of pyrite was determined by quantitative Mössbauer spectroscopy, by measuring the weight loss and the thickness of the unreacted pyrite in the sample. The derived activation energy of about 150 kJ mol⁻¹ corresponds to a destruction rate on the surface of Venus of about 1225 ± 238 days/cm at the top of Maxwell Montes (about 660°K) to about 233 ± 133 days/cm in the plains of Venus (about 740°K). These lifetimes are very short on a geological time scale.

Experimental Mössbauer studies of the weathering of basalt powder [42] under Venus surface conditions suggest that the red colour observed by Pieters et al. [64] at the Venera 9 and 10 landing sites is due to the sub-aerial oxidation of Fe^{2+} -bearing basalt and that hematite, instead of magnetite, is present on the surface of Venus.



Fig. 13. A set of Mössbauer spectra showing the reaction progress for samples heated on the 530°C isotherm. Going from top to bottom, the samples were heated for 2.5, 8, 16, 43, and 97.5 h. The change from pyrite to monoclinic pyrrhotite to hexagonal pyrrhotites is clearly visible in the Mössbauer spectra.

These laboratory results are of course important for the models of Venusian geochemistry, for models of sulfur chemistry in the lower atmosphere of Venus, and for studies of the origin and evolution of the atmosphere of Venus. But it is very important to verify these results by the in situ Mössbauer analysis of the Venusian surface material during a future spacecraft mission to Venus.

3.2.2. Possible mission concepts

After the Russian Venera 9–14 and the US American Magellan spacecraft mission to Venus there are no approved new missions which will go to Venus. There are some plans to propose a Venus mission in the frame of the NASA discovery class mission programme. One of them is the SAGE mission (Discovery Venera Surface-Atmosphere Geochemistry Experiments), with Jim Head III (Brown University, RI) as Principal Investigator. The main part of the mission is to launch a Venera-class lander to a designated target of interest on the surface of Venus. The lander should carry instruments to measure lower atmosphere constituents, surface geology and surface geochemistry and mineralogy. Besides other instruments the use of a Mössbauer spectrometer is in discussion [71,72].

The landing vehicle consists of a pressurized container 1 m in diameter, a scientific instrumentation bay, an antenna, a fixed aerodynamic decelerator, and a landing gear [73]. The total weight of the lander is about 760 kg. The scientific payload, including the soil collection hardware, weighs about 150 kg. During the descent phase acceleration forces up to 160 g will appear. The landing speed is less than 8 m/s.

The lander has a spherical heat-resistant sealed compartment protected from heating by a two layer, high-level thermal insulation system, consisting of rigid, porous and machined high-temperature silica blocks. The inner hull is thermally insulated and isolated from the outer hull. The lander compartment contains the battery, the thermal protection system, and the scientific instruments.

The total surface life time is estimated to be about 2 h. This short lifetime is due to the fact that the lander is heating up inside due to its own internal power consumption. It cannot get rid of the heat due to the excellent thermal insulation. One way to increase the lifetime would be to reduce the total power consumption, which is actually about 200 W, according to the mission concept [73]. The sample material needed for the geochemical and mineralogical analysis will be delivered by a sample acquisition system identical to that used on the Russian Venera 13 and 14 and the Vega 1 and 2 spacecraft. Via a complex system this material is brought inside the compartment, into the soil sample container, a separate vacuum chamber inside the compartment. This sample container is designed to withstand the atmospheric pressure of about 100 bar, and a temperature of about 700°K, in the case the soil sampling device will fail. The other instruments in the inner part of the compartment will not be affected in such a case, and they can finish the mission goal properly. In this way the instruments for geochemical and mineralogical analysis do no have to withstand the ambient temperature and pressure on the Venusian surface.

But there is very limited space available in the soil sample container, mainly due to the safety requirements discussed above. This is of importance for the design of instruments, located in this container.

3.2.3. Possible instrument design

Due to the constraints in available space the Mössbauer instrument should be divided into two parts, one part consisting of the γ - and X-ray detectors, including the preamplifier and the filter amplifier, the source and the Mössbauer drive (let us call this part the "detector head"), and the ADC, the drive control system and the micro-processor (let us call this part the "electronic system"). Only the detector head should be mounted in the soil sample container. The electronic system should be located in the inner compartment of the system itself.

A possible design of the detector head is shown in fig. 14. Also shown are some possible solutions for arranging the Si-PIN-diodes. The final solution will depend of course on the geometry and space available in the real soil sample container. The number and size of the diodes should be chosen in such a way that the solid angle covered is as large as possible. In contrast to the Mars mission power is not a problem, so the number of detector channels could be as high as needed.

For XRF one or two separate detectors will be included. As detectors HgI_2 , small PIN-diodes [74] or CdZnTe [75–77] may be used. Recently with 7 mm² Si-PIN-diodes, slightly cooled (about -30° C), an energy resolution of about 260 eV (at 5.9 keV) has been achieved, which is comparable to the HgI_2 detector included in the Mars94 APX instrument [30].

An increase in temperature causes a decrease in energy resolution and therefore a decrease in the signal to noise ratio. Therefore the detector head should be cooled to keep it at the lowest possible temperature as long as possible. This will also minimize the uncertainty in the velocity signal due to temperature changes of the drive itself.

The electronic system can be operated within a larger temperature range up to may be $60-80^{\circ}$ C, and can be installed in the inner compartment, connected to the detector head via electrical feed throughs. Of course due to temperature variations some components will change their values, which should be taken into account in the design. Due to these complex temperature variations it will be extremely helpful to measure a reference Mössbauer spectrum for a known source sample combination.



Fig. 14. Possible design of the detector head of the Mössbauer spectrometer, consisting of the MB drive and source, the detectors and the preamplifiers. Shown are also some possible solutions for detector arrangements.

3.2.4. General problems and remarks

Probably the biggest problem in using a Mössbauer instrument for a Venus lander mission is the changing temperature of the sample itself. The surface material has a temperature of about 500°C. The soil sample will be delivered within seconds to the sample container, and its temperature probably is only slightly reduced. Of course, the temperature will decrease rapidly by radiation, heat conductivity, and convection, but during this time period due to the temperature dependence of the Debye–Waller factor (f) and the hyperfine parameters, and may be due to phase changes at certain temperatures, the shape of the Mössbauer spectrum might change with temperature (and therefore time!). Because of the limited lifetime of the lander of about 2 h, the main goal is to obtain one Mössbauer spectrum at a certain temperature with sufficient statistical quality.

To obtain this spectrum one should start measuring the Mössbauer spectrum when the sample temperature is more or less constant. On the other hand usually it is very helpful for the identification of Fe-compounds and minerals to conduct temperature dependent measurements even with less statistical quality. For this it will be necessary to collect and transmit the spectra at certain time intervalls, may be every few minutes, depending on the rate of sample cooling. This frequent data transmission might create problems due to the limited downlink capacity. Furthermore the sample temperature is not necessarily uniform. Laboratory tests are necessary to determine how useful such data could be.

To obtain a Mössbauer backscattering spectrum (MBS) of sufficient statistical quality, a source with an activity as high as possible is needed (for limitations see section 2.1). The flight time to Venus is in the order of 120-160 days, which is about half as long as the flight to Mars. Therefore, the loss in intensity and the increase in line width is significantly lower than during a Mars mission. By optimizing the source activity versus increase in line width for a 140 ± 20 days mission duration the statistical quality of the spectrum will be enhanced significantly even without increasing the number of PIN-diodes in comparison to the Mars instrument (see section 3.1.2).

The final conclusion which can be drawn from the discussion above, is that a Mössbauer spectrometer for a mission to Venus is feasible. There is also no doubt, that such data would contribute significantly to the understanding of the evolution of Venus, Earth, Mars and the whole Solar System. But it is completely open whether there will be a Venus lander mission in the near future or not.

3.3. TERRESTRIAL MOON

Since the race to the Moon between the United States and the former Soviet Union, which culminated in the first landing of astronauts on the Moon during the Apollo 11 mission in 1969, there have been no missions to the Moon until the beginning of this year. A small spacecraft, called Clementine, using very advanced technologies, developed partly for the US SDI (so-called "Star Wars") program, was orbiting the Moon at the beginning of this year, mapping the lunar surface nearly completely in various wavelength bands. These investigations allowed to identify areas differing in age and mineralogy.

This mission might be the first step on the way "Back to the Moon", a program which is under investigation at NASA now. Recently also at ESA some activities have been started to initiate a program for Moon science. These programmes include unmanned robotic missions as well as the set up of manned Lunar bases [78]. What are the reasons to think about building lunar bases, where human beings would be permanently present? There are indeed many open scientific questions concerning the evolution of the Moon itself, the system Earth-Moon, and the Solar System, which could be answered only by manned missions. Also the Moon can act as the most ideal platform for different kinds of observatories. On the Moon there is no atmosphere which on Earth sets a certain limit for optical astronomy as well as for investigations in other wavelength bands. For instance radio and gamma ray astronomy would find optimal conditions for operation on the Lunar surface, especially on the back side. Also an idea of building a giant accelerator around the equator of the Moon has been advanced [79]. No vacuum system is required. Only the deflecting magnets and the accelerating stations would be needed.

A Lunar base could also serve as an intermediate station on the way to other targets in the Solar System, for unmanned as well as manned missions. Less propellant is needed in respect to a launch from the Earth. Finally people are thinking about using Lunar resources to compensate limitations in terrestrial resources [78].

The feasibility of all these plans (some of them sound very futuristic) depends strongly on the possibility of producing oxygen on the Moon. Oxygen will be used as propellant (together with hydrogen), and it is needed for the life support system of a Lunar base. Different research groups and companys have investigated how to extract oxygen from Lunar material [78]. A very promising mineral for this issue seems to be the mineral ilmenite, which is present in Lunar basalt, soils, and rocks, with a natural abundance of about 5 wt% (in average). It has been demonstrated recently that oxygen can be extracted in significant amounts from Lunar material by reducing ilmenite. For these experiments 10 kg of Lunar material (Apollo sample 70035) containing 25% ilmenite, have been used [81]!

To use ilmenite as a source for oxygen production would need knowledge about locations on the Lunar surface with a high abundance of this mineral. This means that as on Earth some kind of exploration is required to find these ilmenite rich places. Here Mössbauer spectroscopy may play an important role [80]. Ilmenite can be easily determined by MBS due to its characteristic pattern (see for instance ref. [81]). Having a Mössbauer instrument mounted on a Lunar rover would allow to search for ilmenite very effectively. Also the absolute amount of this mineral could be determined if the MBS will include XRF capabilities, too (see section 3.1.2). Furthermore, MBS could be used to monitor in situ the degree of reduction of ilmenite during the oxygen production process. Besides the use of Mössbauer spectroscopy for the exploitation of Lunar resources such an instrument could be used in unmanned missions to the Moon, dedicated specifically for basic research purposes. It has been demonstrated during the analysis of the Lunar material, which have been brought back to Earth by the Apollo missions, that Mössbauer spectroscopy is extremely helpful for the determination of minerals present in these samples [82].

In comparison to missions to Venus or Mars (or even other missions to more distant solar bodies) the experimental constraints are not very severe in Lunar missions. The flight duration is in the order of days. Therefore problems concerning the maximal source activity only would arise if the mission on the Lunar surface lasts in the order of one half life of 57 Co (about 260 days) or longer. There also should be enough power available to operate experiments in an optimal way. Mass restrictions should not be as severe as in missions to more distant targets. Therefore a very capable Mössbauer instrument could be sent to the Moon, from which a lot of very interesting data would be expected.

3.4. COMETS

Comets and asteroids are believed to represent the most primitive solar system bodies. They are assumed to have kept a record of the chemical processes occurring during the early stages of the solar system. It is assumed that comets have been formed at large heliocentric distances and kept there at low temperatures. Some of these are occasionally transferred to trajectories crossing the inner part of the Solar System, sometimes coming close to planets (e.g. the Earth).

Cometary material is assumed to contain presolar grains and condensates from the protosolar nebula, from which the planetesimals and afterwards larger planetary bodies have formed. Therefore, cometary material represents the oldest material available in the Solar System. Material from asteroids in this point of view is in a stage of evolution inbetween cometary and planetary material. It is found that asteroids with relatively large distances to the Sun have spectral similarities with cometary nuclei. This is especially the case for the most distant asteroid Chiron, with an orbit outside the planet Saturn. This asteroid is often considered as a "giant" comet nucleus [83].

The trademark of comets is their gas activity, leading to more or less pronounced tails. Models of cometary nuclei were based on the idea of some kind of a "dirty snowball" (icy conglomerates) [84]. But the recent space missions to comet P/Halley, and other observations during the last years have shown that at least P/ Halley and other short period comets are extensively covered by refractory material. The relative abundance of dust (refractory material) at least near the surface of a comet is large (nearly 50%). It is now considered probable that cometary nuclei are dominated by this refractory material, consisting mainly of silicates and organic material. Instead of a dirty snowball a comet nucleus seems to be more like an "icy dustball" (see fig. 15) [83]. But what is the composition of such a comet nucleus, which is supposed to resemble primitive solar system material?

Extraterrestrial material available on Earth, divided into two major classes, provide the actual data base for what is believed to be primitive solar system material: (1) chondrites and (2) interplanetary dust. Chondrites are a special class of meteorites, which are believed to originate mainly from the main belt of asteroids. Of extreme interest is the subclass of carbonaceous chondrites, which is considered to be the most primitive class of meteorites. Carbonaceous chondrites may be identical with cometary material (probably in a more processed stage).

Carbonaceous chondrites (CI, CM) are the only meteorites, where magnetite has been found [86–88], with exception from the SNC meteorites, which are supposed to originate from the planet Mars [7,89–92]. Furthermore, the five CI's have an elemental composition that matches very closely the condensable portion of the Sun. To establish whether this class of meteorites resembles really cometary material, in a more processed stage, would be very important. If CM's and CI's are really of cometary origin, a significant amount of cometary material would be available on Earth. In this case the question of having a very expensive sample return mission to a comet would not arise immediately.

The main contributions of Mössbauer spectroscopy to the understanding of the origin and evolution of the solar system itself, and its present status, would be:

- determination of whether magnetite (Fe₃O₄) is present on the surface of a comet nucleus (in the dust material) or not;
- identification of the Fe bearing minerals;
- identification of the oxidation state of iron, which is very important for different models on the evolution of the solar system.



Fig. 15. Macroscopic model of the near surface zone of a comet nucleus at a potential landing site (by courtesy of ESA [85]).

3.4.1. Main characteristics of a mission to a comet and their implications to a Mössbauer instrument

The characteristics of a mission to a comet of course depend on the target itself. Different comets are very different in minimum distances to Earth (or the Sun). They do have very different orbiting times. Also a comet with a rather well known trajectory should be chosen to allow a sufficiently good targeting of the spacecraft. According to the Rosetta mission studies [83] reachable targets are shortperiod comets with low inclination with respect to the ecliptic plane and perihelion radii near 1 astronomical unit (AU). Different possible cometary targets have been studied under different assumptions (see the Rosetta report [83]). A list of 11 possible targets has been determined, with launches between the year 2002 and 2004, and flight times between 5 and 10 years (arrival at the comet).

Having a closer look at the different possible targets (please note: the Rosetta mission has been approved by ESA in 1994, which means that this mission really will go!) a number of serious constraints for the spacecraft, the lander module and a possible Mössbauer instrument could be identified, which partly are described in the Rosetta report [83]. One of the most fascinating and difficult tasks of the mission itself, after approaching the comet and getting into a stable orbit around the nucleus, which has nearly zero gravity, is the landing of the surface probe. The diameter of a typical comet nucleus is in the order of a few kilometers (e.g. P/Hallev). Due to the very low gravity the speed during landing has to be kept as small as possible to minimize the probability of a rebound, which could lead to the escape of the surface package from the comets gravity field. Different techniques are in discussion to land the surface probe. One of them is to have some kind of a cork-screw mounted on the probe [93,94]. By bringing the probe itself into well defined rotation, during the landing the probe will fix itself by screwing into the surface of the comet. But there are a lot of open questions, for instance nobody knows about the structure of the surface material. At the moment is has not been decided how the lander will be brought to the surface.

The main constraint for the Mössbauer instrument itself is the flight time of about 5 to 10 years. The most probable targets are the comets Schwassmann–Wachmann 3 and Wirtanen with flight times for the spacecraft of about 5 and 8 years, respectively. Because of the half-life-time of 57 Co of about 260 days there would be a reduction in source intensity of about a factor of 130 and 2000 for the missions to Schwassmann–Wachmann 3 and Wirtanen, respectively. The amount of Fe present in the surface material of comets is not known. This makes it difficult to estimate the measuring time needed to get a Mössbauer backscattering spectrum within the expected lifetime of the lander. Furthermore there are different options of landers in discussion today, short living (up to about 1 day) and long living stations (up to 10 days). Assuming a relative abundance of iron of about 10% in weight (comparable to earth like planets), the 57 Co Mössbauer source activity, needed at launch time, can be estimated taking into account the mission constraints itself:

Version (a): 5 years of flight time (Schwassmann-Wachmann 3)

- short living lander; available measuring time about 10 h; source activity at launch: about 3-5 Ci;
- long living lander; available measuring time about 50 h; source activity at launch: about 1 Ci.
- Version (b): 8 years of flight time (Wirtanen)
- short living lander; available measuring time about 10 h; source activity at launch: 40-50 Ci;
- long living lander; available measuring time about 50 h; source activity at launch: about 10 Ci.

The needed source activities for a mission to a comet are rather high. Due to limitations to about 1 Ci/cm^2 a source with a rather large dimension is needed. This will not allow to use a standard source-sample-detector geometry as is the case of the "Mars" instrument (see fig. 7). To limit the cosine smearing to a tolerable value one has to limit the maximum emission angle. This could be done by using a honeycomb structure for the collimator.

To improve the signal to noise ratio the energy resolution of the detector should be improved. There are several possibilities which seem to be feasible within the next few years. First of all Si-PIN detectors with much better energy resolution have been announced recently [74]. Very promising results using CdZnTe (CZT) detectors have been published [75–77]. CZT has the advantage of high detection efficiency (nearly 1 for energies below 15 keV), and a small Compton scattering cross section. This material can be handled relatively easy, in contrast to the HgI₂, which also has a very good energy resolution and a small Compton cross section. But there are still problems in handling the material [95]. Having these types of detectors available with sufficiently large sensitive area, which is in the order of 20 to 100 mm², the sensitivity of the Mössbauer instrument would be improved significantly.

One also has to think of using a transmission geometry instead of the backscattering geometry, proposed for space applications. This, of course, would need sample preparation, but in the case of a mission to a comet this might be easier to do than to use those very strong sources. Both possibilities will be studied very carefully in the near future.

The long duration of the Rosetta mission is due to the fact that the spacecraft needs some gravity assist by the Earth, Venus, and also Mars, to reach the comet, because for launch a European Ariane 5 rocket will be used. The use of a more powerful American or Russian launcher would allow a more direct pass to the comet. The flight duration would be significantly shorter than using the European launcher. In this case to build a Mössbauer spectrometer would be much easier.

3.5. OTHER TARGETS

Besides the terrestrial Moon, Venus, Mars and the comets there are, of course,

334

a lot of other solid bodies present in our solar system. All of them are of interest for planetary science. One of the planets not very well known is Mercury. It is the planet closest to the Sun, and therefore there is a big interest in its chemical and mineralogical composition. The flight time needed to go to Mercury is not critical for a Mössbauer instrument. This is not the case for the big planets Jupiter, Saturn, Uranus and Neptun. A trip to these planets needs a relatively long time. As in the case of the mission to a comet it will depend strongly on the capabilities of the launcher whether one really would consider seriously sending a Mössbauer instrument to one of the planets. Furthermore, the surface environmental conditions make it nearly impossible for a lander to survive a time period long enough to allow measurements. Because of this the only accessible targets in this area of the solar system might be the moons of these planets.

Very interesting from the point of view of evolution of the Solar System are asteroids (see section 3.4). Some of these bodies are occasionally approaching very close to the Earth. Therefore, only relatively little time is needed to go to an asteroid. Because of the low gravity the problem of how to land a surface probe has to be solved. This is similar to a mission to a comet (see section 3.4).

4. Conclusion and outlook

By now five years have passed since the first realistic proposals for a Mössbauer spectrometer for space applications were made [13,16]. We have joined the Mars96 project about four years ago and we experienced that the method of Mössbauer spectroscopy was not well known in the planetary science community. This situation has changed significantly and MB spectroscopy is now widely accepted as a new tool for this field of science. As shown in this paper a certain number of space missions have a Mössbauer instrument in the payload, or have at least considered seriously to include such an instrument. Therefore, there is a high probability that a Mössbauer spectrometer will leave our planet within the next few years, because sample return missions, which are also under consideration, are far beyond the actual possibilities of financial resources.

There is a big and controversial discussion on whether one should have a sample return mission. Bringing samples to laboratories on the Earth, or maybe to a future space station, has, of course, the advantage that these samples can be analysed with much higher accuracy than in situ on the surface of a solar system body. This is valid also for a Mössbauer spectrometer. But will samples be delivered to the labs really without any changes in their properties (e.g. oxidation)?

Besides the development of the instrument a number of laboratories have started programs on so-called Mars sample analogs, which are not only studied by the MB technique. Correlations of the MB results to magnetic properties, reflectance spectroscopic data etc. are most important [32–39,1,47]. Similar studies are now performed for the weathering of Venus surface material [40–43,65]. The knowledge gained from all these activities will play a decisive role when data are finally returned from solar system targets as for instance Mars or Venus. Finally, Mössbauer spectroscopy might help to understand the natural laws which produced the world in which we live.

Acknowledgement

This work is funded by the German Space Agency (DARA). The MIMOS for Mars96 is developed in cooperation with the Space Research Institute (IKI), Moscow, Russia, the University of Copenhagen, Denmark, and the CNRS, Toulouse, France. Fruitful and helpful discussions with Dr. R. Rieder, Max-Planck-Institute for Cosmochemistry, Mainz, Dr. Oleg Prilutskii, Dr. E. Evlanov, and Dr. V. Khromov, Space Research Institute Moscow, Russia, Professor J.M. Knudsen, Dr. M.B. Madsen and Dr. L. Vistisen, University of Copenhagen, Dr. R.V. Morris, Johnson Space Center, Houston, Texas, USA, Professor D.G. Agresti, University of Alabama at Birmingham, USA, Professor B. Fegley Jr., Washington University, St. Louis, USA, and Dr. C. d'Uston, CNRS, Toulouse, France, are acknowledged very much.

References

- J.M. Knudsen, M.B. Madsen, M. Olsen, L. Vistisen, C.B. Koch, S. Mørup, E. Kankeleit, G. Klingelhöfer, E.N. Evlanov, V.N. Khromov, LM. Mukhin, O.F. Prilutskii, B. Zubkov, G.V. Smirnov and J. Juchniewicz, Hyp. Int. 68 (1991) 83.
- [2] G. Klingelhöfer, J. Foh, P. Held, H. Jäger, E. Kankeleit and R. Teucher, Hyp. Int. 71 (1992) 1449.
- [3] E. Kankeleit, J. Foh, P. Held, G. Klingelhöfer and R. Teucher, Hyp. Int. 90 (1994) 107.
- [4] W.M. Irvine, The Planetary Report 7 (6) (1987) 6.
- [5] J.M. Knudsen, Hyp. Int. 47 (1989) 3.
- [6] The Comet Rendezvous Asteroid Flyby Mission. A Search for our Beginnings, National Aeronautics and Space Administration (NASA) and Jet Propulsion Laboratory, CALTECH, Pasadena, CA.
- [7] T.J. Wdowiak and D.G. Agresti, Nature 311 (1984) 140.
- [8] M.B. Madsen, S. Mørup, T.V.V. Costa, J.M. Knudsen and M. Olsen, Hyp. Int. 41 (1988) 827.
- [9] C.L. Herzenberg and D.L. Riley, Science 167 (1970) 683.
- [10] A.H. Muir Jr., R.M Housley, R.W. Grant, M. Abdel-Gawad and M. Blander, Science 167 (1970) 688.
- [11] H. Fernandez-Moran, S.S. Hafner, M. Ohtsuki and D. Virgo, Science 167 (1970) 686.
- [12] P. Gay, G.M. Bancroft and M.G. Brown, Science 167 (1970) 626.
- [13] J. Galazkha-Friedman and J. Juchniewicz, Martian Mössbauer Spectrometer MarMös, Project Proposal, Space Research Center, Polish Academy of Sciences, February 1989.
- [14] J. Foh, P. Held, H. Jäger, E. Kankeleit, G. Klingelhöfer and U. Imkeller, Ann. Geophys. suppl. Vol. 9 C452 (1991).
- [15] E.N. Evlanov, L.M. Mukhin, O.F. Prilutski, G.V. Smirnov, J. Juchniewicz, E. Kankeleit, G. Klingelhöfer, J.M. Knudsen and C. d'Uston, Lunar Planet. Sci. XXII (1991) 361.

- [16] R.V. Morris, D.G. Agresti, T.D. Shelfer and T.J. Wdowiak, Lunar Planet. Sci. XX (1989) 721.
- [17] T.D. Shelfer, M.M. Pimperl, D.G. Agresti, E.L. Wills and R.V. Morris, Lunar Planet. Sci. XXII (1991) 1229.
- [18] D.G. Agresti, E.L. Wills, T.D. Shelfer, J.S. Iwanczyk, N. Dorri and R.V. Morris, Lunar Planet. Sci. XXI (1990) 5.
- [19] E.N. Evlanov, V.A. Frolov, O.F. Prilutski, A.M. Rodin and G.V. Veselova, Mössbauer Spectrometer for Mineralogical Analysis of the Mars Surface: Mössbauer Source Considerations, Internal Report, Space Research Institute (IKI), Moscow, Russia.
- [20] E.N. Evlanov, V.A. Frolov, O.F. Prilutski, A.M. Rodin, G.V. Veselova and G. Klingelhöfer, Lunar Planet. Sci. XXIV (1993) 459.
- [21] A.W. Gummer, Nucl. Instr. Meth. B 34 (1988) 224.
- [22] G. Klingelhöfer, U. Imkeller, E. Kankeleit and B. Stahl, Hyp. Int. 71 (1992) 1445.
- [23] E. Kankeleit, Rev. Sci. Instr. 35 (1964) 194.
- [24] E. Kankeleit, in: Proc. Int. Conf. on Mössbauer Spectroscopy, Vol. 2, Cracow (1975) 43.
- [25] R. Teucher, Miniaturisieter Mössbauerantrieb, Diploma Thesis, TH Darmstadt, Inst. F. Nuclear Physics, Germany (1994).
- [26] S. Margulies and J.R. Ehrman, Nucl. Instr. Meth. 12 (1961) 131.
- [27] Ch. Weinheimer, M. Schrader, J. Bonn, Th. Loeken and H. Backe, Nucl. Instr. Meth. A 311 (1992) 273.
- [28] P. Held, R. Teucher, G. Klingelhöfer, J. Foh, H. Jäger and E. Kankeleit, Lunar Planet. Sci. XXIV (1993) 633.
- [29] R. Rieder, private communication on developments of AMPTEC, USA.
- [30] T.E. Economou, J.S. Iwanczyk and R. Rieder, Nucl. Instr. Meth. A 322 (1992) 633.
- [31] K.J. McCarthy and A. Wells, in: Proc. SPIE Technical Symposium, San Diego, CA, July 1992.
- [32] J.M. Knudsen, S. Mørup and J. Galzkha-Friedman, Hyp. Int. 57 (1990) 2231.
- [33] R.V. Morris and H.V. Lauer Jr., J. Geophys. Res. 95 (1990) 5101.
- [34] J.L. Bishop, C.M. Pieters and R.G. Burns, Lunar Planet. Sci. XXIV (1993) 115.
- [35] J.L. Bishop, C.M. Pieters, S.F. Pratt and W. Patterson, Lunar Planet. Sci. XXIV (1993) 117.
- [36] J.L. Bishop, C.M. Peters and R.G. Burns, Geochim. Cosmochim. Acta 57 (No. 19), in press.
- [37] A. Banin, D.F. Blake and T. Benshlomo, Lunar Planet. Sci. XXII (1991) 49.
- [38] A. Banin, B.C. Clark and H. Wänke, in: Mars, eds. H.H. Kieffer, B.M. Jakosky, C.W. Snyder and M.S. Matthew (The University of Arizona Press, Tucson, 1992).
- [39] J.F. Bell III, T.B. McCord and P.D. Owensby, J. Geophys. Res. 95 (1990) 14447.
- [40] B. Fegley Jr. and K. Lodders, Lunar Planet. Sci. XXIV (1993) 467.
- [41] G. Klingelhöfer, B. Fegley Jr. and K. Lodders, Lunar Planet. Sci. XXV (1994) 707.
- [42] B. Fegley Jr., G. Klingelhöfer, R.A. Brackett and N. Izenberg, Meteoretics 29 (1994) 465.
- [43] B. Fegley, Jr., K. Lodders, A.H. Treiman and G. Klingelhöfer, The rate of pyrite decomposition on the surface of Venus, Icarus 1994, submitted.
- [44] B. Fegley, Jr. and A.H. Treiman, in: Venus and Mars: Atmospheres, Ionospheres, and Solar Wind Interactions, Geophysical Monograph 66 (American Geophysical Union, Washington, 1992).
- [45] Mars-94, Unmanned Spacecraft Mission to Mars (brief description), January 1991, Space Research Inst., Vernadsky Inst. Geochemistry and Analytic chemistry, USSR Academy of sciences; Babakin Center, USSR.
- [46] Scientific results of the Viking Project, J. Geophys. Res. 82 (28) (1977).
- [47] R.V. Morris, D.G. Agresti, H.V. Lauer Jr., J.A. Newcomb, T.D. Shelfer and A.V. Murali, J. Geophys. Res. 94 (1989) 2760.
- [48] J.M.D. Coey, S. Mørup, M.B. Madsen and J.M. Knudsen, J. Geophys. Res. 95 (B9) (1990) 14423.
- [49] M.H. Carr, The Surface of Mars (Yale University Press, New Haven, 1981).

- [50] R. Burns and A. Banin, eds., Workshop on Chemical Weathering on Mars, LPI Tech. Rpt. 92-04, Part 1 (Lunar and Planetary Institute, Houston, 1992).
- [51] R. Burns and A. Banin, eds., Workshop on Chemical Weathering on Mars, LPI Tech. Rpt. 92-04, Part 2 (Lunar and Planetary Institute, Houston, 1993).
- [52] D.G. Agresti, R.V. Morris, E.L. Wills, T.D. Shelfer, M.M. Pimperl, M. Shen, B.C. Clark and B.D. Ramsey, Hyp. Int. 72 (1992) 285.
- [53] O. Prilutskii, Space Research Institute (IKI), Moscow, internal report from Minsk (1990).
- [54] Technical Requirements on Providing the Planetary Quaratine during Conduction of the Mars 94/96 Missions, Internal Report of the Centre National d'Etudes Spatiales (CNES), Toulouse, France, April 1993.
- [55] M.B. Madsen, J.M. Knudsen, L. Vistisen and R.B. Hargraves, Lunar Planet. Sci. XXIV (1993) 917.
- [56] J.M. Knudsen, H.C. Ørsted Institute, University of Copenhagen, Denmark, private communication.
- [57] G. Klingelhöfer and E. Kankeleit, Internal Proposal to Russian Space Agency IKI for an additional experiment using magnetic separation capabilities of a magnet array (1992).
- [58] P. Baltes, J. Foh, H. Jäger, E. Kankeleit, Ch. Müntz, H. Oeschler, S. Sartorius, A. Wagner and the KaoS Collaboration, A New Modular Transputer-Based Data Acquisition System, GSI Scientific Report (1990) p. 346.
- [59] P. Baltes, Diploma Thesis, Institute for Nuclear Physics, TH Darmstadt, Germany (1993).
- [60] MARSNET, a Network of Stations on the Surface of Mars, ESA Publication SCI (91) 6.
- [61] B. Pavri et al., Steep-sided domes on Venus: characteristics, geologic setting, and eruption conditions from Magellan data, J. Geophys. Res. Planets (1992), in press.
- [62] V. Baker et al., Channels and valleys on Venus: preliminary analysis of Magellan data, J. Geophys. Res. Planets (1992), in press.
- [63] G. Pettengill et al., Venus surface radio-thermal emission as observed by Magellan, J. Geophys. Res. Planets 97 (1992) 13091.
- [64] C. Pieters, J.W. Head, W. Patterson, S. Pratt, J. Garvin, V.L. Barsukov, A.T. Basilevsky, I.L. Khodakovsky, A.S. Selivanov, A.S. Panofilov, Yu.M. Getkin and Y.M. Narayeva, Science 234 (1986) 1379.
- [65] B. Fegley Jr., N.H. Treiman and V.L. Sharpton, Proc. Lunar Planet. Sci. Conf. 22 (1992) 3.
- [66] U. von Zahn, S. Kumar, H. Niemann and R.G. Prinn, in: Venus, eds. D.M. Hunten, L. Colin, T.M Donahue and V.I. Moroz (University of Arizona Press, Tucson, 1983) pp. 299–430.
- [67] R.G. Prinn, in: The Photochemistry of Atmospheres, ed. J.S. Levine (Academic Press, New York, 1985) pp. 281-336.
- [68] G.H. Pettengill, P.G. Ford and S. Nozette, Science 217 (1982) 640.
- [69] G.H. Pettengill, P.G. Ford and B.D. Chapman, J. Geophys. Res. 93 (1988) 14881.
- [70] G.H. Pettengill, P.G. Ford, W.T.K. Johnson, P.K. Raney and L.A. Soderblum, Science 252 (1991) 260.
- [71] J.W. Head III, Brown University, RI, USA, private communication.
- [72] J. Bradley, Jet Propulsion Laboratory (JPL), Pasadena, CA, USA, private communication.
- [73] J.W. Head III et al., Discovery Venera Surface-Atmosphere Geochemistry Experiments (SAGE), NASA Discovery Missions Workshop, Concept No. 55, September 1992.
- [74] AMPTEK Inc. product information on X-ray detector with a 7 mm² Si-PIN-Diode (XR-100TR);
 - R. Rieder, MPI Cosmochemie, Mainz, Germany, private communication (August 1994); J. Pantazis, AMPTEK Inc., Bedford, MA, USA, private communication (August 1994).
- [75] J.F. Butler, F.P. Doty and C.L. Lingren, IEEE Trans. Nucl. Sci. 39 (1992) 605.
- [76] A. Niemelae and H. Sipilae, Outokumpu Instruments Oy, Riihitontuntie 7C, FIN-02201 Espoo, Finland.

- [77] AMPTEK Inc. product information on CdZnTe detector system: XR-100TR; Evaluation of CdZnTe Detectors for Soft X-ray Applications, R. Rieder, MPI Cosmocheie, Mainz, Germany, private communication (August 1994);
 - John Pantazis, AMPTEK Inc., Bedfore, MA, USA, private communication (August 1994).
- [78] W.W. Mendell, ed., Lunar Bases and Space Activities of the 21st Century (Lunar and Planetary Institute, Houston, 1985).
- [79] E. Teller, in: Lunar Bases and Space Activities of the 21st Century, ed. W.W. Mendell (Lunar and Planetary Institute, Houston, 1985).
- [80] R.V. Morris, NASA Johnson Space Center, Houston, Texas, USA, private communication.
- [81] M.A. Gibson, C.W. Knudsen, D.J. Brueneman, H. Kanamori, R.O. Ness, L.L. Sharp, D.W. Brekke, C.C. Allen, R.V. Morris, L.P. Keller and D.S. Mckay, Lunar Planet. Sci. XXIV (1993) 531.
- [82] S.S. Hafner, in: Mössbauer Spectroscopy, Topics in Applied Physics, Vol. 5, ed. U. Gonser (Springer, Berlin, 1975).
- [83] ROSETTA Comet Rendezvous Mission, European Space Agency (ESA), report SCI(93)7, September 1993.
- [84] F.L. Whipple, Astrophys. J. 111 (1950) 375;
 F.L. Whipple, Astrophys. J. 113 (1950) 464.
- [85] Stöffler et al., in: ROSETTA Comet Rendezvous Mission, European Space Agency (ESA), report SCI(93)7, September 1993.
- [86] B. Mason and Wiik, Am. Mus. Novitates 2106 (1962) 1.
- [87] B. Mason, Space Sci. Rev. 1 (1963) 621.
- [88] P. Ramdohr, J. Geophys. Res. 68 (1963) 201.
- [89] M.B. Madsen, J.M. Knudsen, L. Vistisen and H.G. Jensen, in: The Environmental Model of Mars, ed. K. Szegö, COSPAR Colloquia Vol. 2, Jan. 1990.
- [90] T.E. Bunch and A.M. Reid, Meteoritics 10 (1975) 303.
- [91] E.M Stolper and H.Y. McSween Jr., Geochim. Cosmochim. Acta 43 (1979) 1475.
- [92] M.B. Madsen, M. Olsen, J.M. Knudsen, D. Petersen and L. Vistisen, Lunar Planet. Sci. XXIII (1992) 825.
- [93] H. von Hoerner, vH&S Space Systems, Germany, private communication (1994).
- [94] H. Rosenbauer, Max-Planck Institute for Aeronomie, Kathlenburg-Lindau, Germany, private communication.
- [95] R. Rieder, MPI Cosmochemie, Mainz, Germany, private communication.