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# Field-portable Mössbauer spectroscopy on Earth, the Moon, Mars, and beyond

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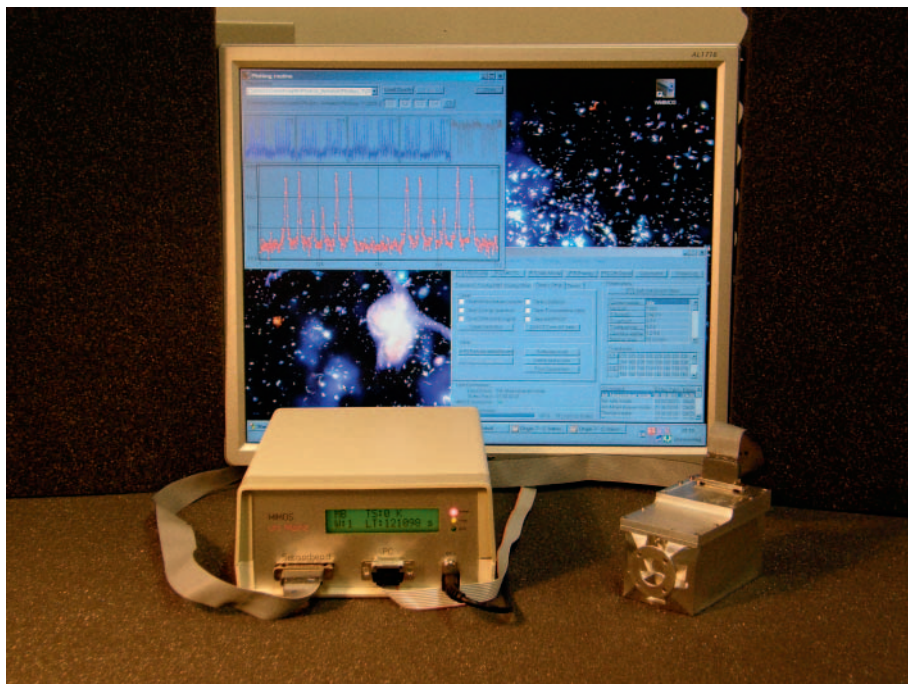
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**ABSTRACT:** Iron occurs naturally as Fe<sup>2+</sup>, Fe<sup>3+</sup>, and, to a lesser extent, as Fe<sup>0</sup>. Many fundamental (bio)geochemical processes are based on redox cycling between these oxidation states. Mössbauer spectroscopy provides quantitative information about the distribution of Fe among its oxidation states, identification of Fe-bearing phases, and relative distribution of Fe among those phases. Portable, miniaturised Mössbauer spectrometers were developed for NASA's Mars Exploration Rovers (in operation since 2004) and provide a means for non-destructive, *in-situ* field investigations. On Mars, these instruments provided evidence for aqueous activity with implications for habitability, were applied in geological mapping of the landing sites, and helped to identify meteorites, for example. On Earth, they were used in field studies of green rust, the identification of air pollution sources, or the study of archaeological artefacts. Their application to *in-situ* resource utilisation (ISRU) on the Moon has been demonstrated in a recent NASA field test of hardware for oxygen production. A new detector system in an advanced version of these instruments is based on Si Drift Detectors and permits the simultaneous acquisition of X-ray fluorescence spectra to determine elemental compositions.

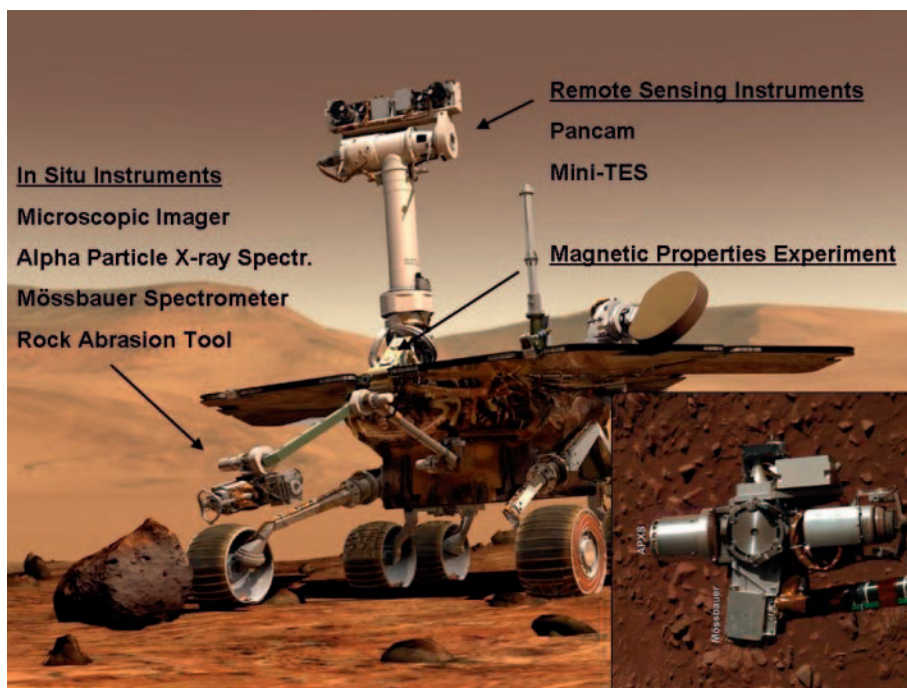
**KEYWORDS:** *Fe (bio)geochemistry, archaeometry, in-situ resource utilisation (ISRU), non-destructive*

Iron is one of the most abundant elements in the universe and ubiquitous in materials of geochemical interest. Mössbauer (MB) spectroscopy is an established laboratory technique and a powerful tool to study Fe-bearing substances, providing quantitative information about the distribution of Fe among its oxidation states, identification of Fe-bearing phases, and relative distribution of Fe among those phases. Surface materials on Mars are enriched in Fe relative to Earth; the Red Planet's colour is a result of Fe oxide pigments. This motivated the development of a miniaturised MB spectrometer suitable for space applications. The resulting instrument, dubbed MIMOS II (Fig. 1; Klingelhöfer *et al.* 2003), is part of the payload of NASA's two Mars Exploration Rovers (MER; Fig. 2), which are investigating the surface of Mars since January 2004. MIMOS II is set up in backscattering geometry (Fig. 3) in order

to avoid complicated sample preparation procedures, i.e. the preparation of powders or thin slices necessary for analyses with standard laboratory MB transmission setups, and thus also becomes a non-destructive analytical tool. Currently, Si Drift Detectors (SDD; Lechner *et al.* 1996) are implemented in the instrument design (e.g., Klingelhöfer *et al.* 2008). Their enhanced energy resolution relative to the previously used Si-PIN detectors increases the signal-to-noise ratio and thus decreases measurement times. In addition, they enable the simultaneous acquisition of X-Ray Fluorescence (XRF) spectra for elemental analysis also of lighter elements down to Mg. In the following we will briefly describe this advanced version of the instrument, MIMOS IIa, which combines MB and XRF spectroscopy. Then we will discuss examples from diverse applications of portable MB spectroscopy on Earth, the Moon,



**Fig. 1.** The main components of the miniaturised Mössbauer spectrometer are the electronics board in the box on the lower left and the sensorhead on the lower right. A PC is necessary to start and stop measurements, and to read out and evaluate the obtained Mössbauer spectra.



**Fig. 2.** Artist's impression of the Athena payload of the two NASA Mars Exploration Rovers, Spirit and Opportunity. Inset is an image of the instruments on the robotic arm obtained with Spirit's Pancam on sol 287 of her mission: The Alpha Particle X-ray Spectrometer (pointing to the left), the Mössbauer spectrometer (down), the Rock Abrasion Tool (right), and the Microscopic Imager (up). A sol is a day on Mars, slightly longer than 24 hrs. The two Panoramic Camera (Pancam) 'eyes' on top of the mast are at a height of approximately 1.5 m. Background image: NASA/JPL/Cornell. Inset: [http://marswatch.astro.cornell.edu/pancam\\_instrument/images/False/Sol287A\\_P2141\\_1\\_False\\_L456.jpg](http://marswatch.astro.cornell.edu/pancam_instrument/images/False/Sol287A_P2141_1_False_L456.jpg).

Mars, and beyond. For a detailed introduction to MB spectroscopy and its use in geochemistry, we refer the interested reader to available textbooks and reviews, for example by Bancroft (1973), Hawthorne (1988), Mitra (1992), Burns (1993), McCammon (1995), Murad & Cashion (2004) or Gütlich & Schröder (2010). Potts & West (2008) have edited a volume on diverse applications of portable XRF spectroscopy.

### MIMOS IIA INSTRUMENT DESCRIPTION

The miniaturised Mössbauer spectrometer MIMOS II has two main components, an electronics board and a sensor head (Fig. 1). The electronics board contains power supplies, a central processing unit, memory, and associated support electronics.

The sensor head contains the velocity transducer or drive, which vibrates the MB sources, and the detectors and amplifiers (Fig. 4). The instrument is set up in backscattering geometry (Fig. 3), which renders sample preparation unnecessary and thus allows for non-destructive measurements. One simply needs to point the front of the sensor head towards the sample of interest and bring the instrument in contact with or close proximity to it (e.g. inset in Fig. 3). The main detectors at the front end are shielded from direct irradiation by the main MB source with the help of a collimator (Fig. 4), which also limits the field of view of the instrument to *c.* 1.4 cm in diameter. The source of the characteristic 14.4 keV  $\gamma$ -rays for the MB experiment is  $^{57}\text{Co}$  in Rh matrix, which decays via electron capture to  $^{57}\text{Fe}$ . Figure 5 shows a simplified decay scheme.



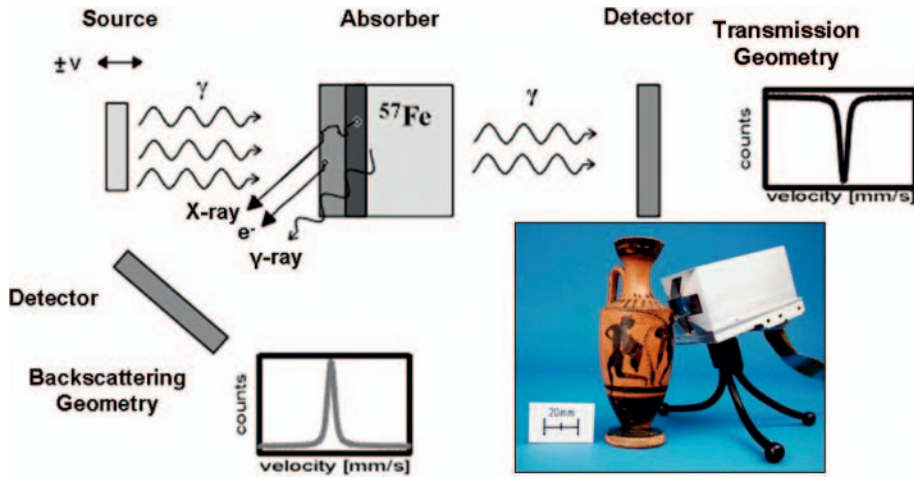


Fig. 3. Mössbauer experiments can be set up in backscattering geometry as in MIMOS IIa or standard transmission geometry. Backscattering geometry allows for non-destructive measurements (see inset, for example) because the preparation of thin slices or powders to let radiation pass through the sample is rendered unnecessary. Furthermore, secondary deexcitation processes can be detected which allow for depth-selective measurements.

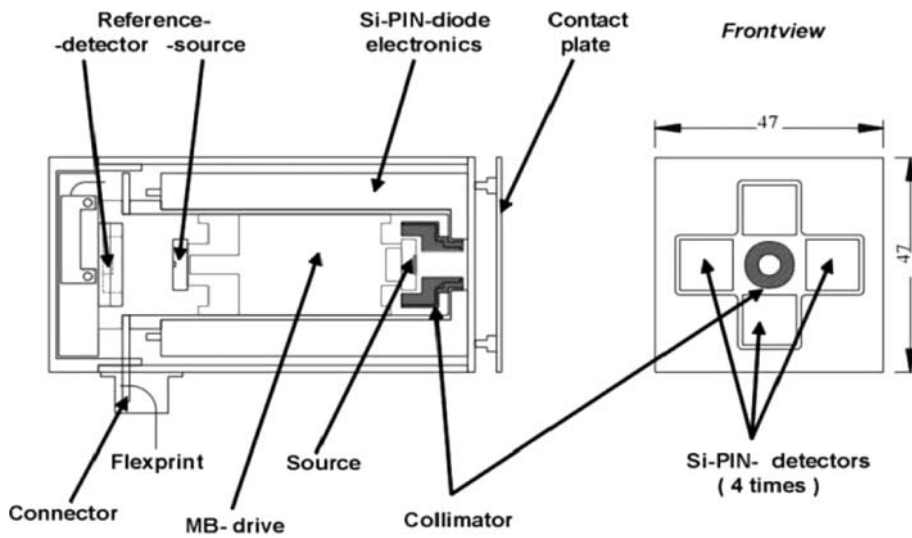


Fig. 4. This schematic drawing shows the main components of the MIMOS II sensor head. Dimensions are given in mm.

MIMOS II can simultaneously collect separate MB spectra from the detection of reemitted 14.4 keV  $\gamma$ -rays and secondary 6.4 keV X-rays. As a result of the difference in energy and therefore different attenuation coefficients, the comparison of 6.4 keV and 14.4 keV MB spectra allows for depth selective investigations, for example of weathering rinds (e.g. Fleischer *et al.* 2008). A second, weaker MB source can be installed on the back end of the velocity transducer (Fig. 4). Together with a well-known reference target such as  $\alpha$ -Fe foil and a detector, it provides a transmission experiment for real-time calibration. MIMOS II needs a 12 V power supply, which is connected to the electronics box. A car battery, generator or solar cell panel can be used in the field. A PC is necessary to start and stop measurements as well as to read out and evaluate MB spectra. The PC is connected to the electronics box via a serial cable. The serial cable can also be replaced by a wireless Bluetooth connection (cf. Fig. 14). Electronics board and sensor head together weigh approximately 900 g, the sensor head alone 400 g. Klingelhöfer *et al.* (2003) provide a detailed description of the instrument.

The most significant change in MIMOS IIa, an advanced version of the instrument, is the implementation of SDDs instead of Si PIN diodes (Fig. 6). Experience with SDDs has already been gained with the Alpha Particle X-ray Spectrometer (APXS), which is also part of the payload of the Mars Exploration Rovers (Fig. 2; Rieder *et al.* 2003) as well as the ROSETTA mission, launched in 2004 and scheduled to

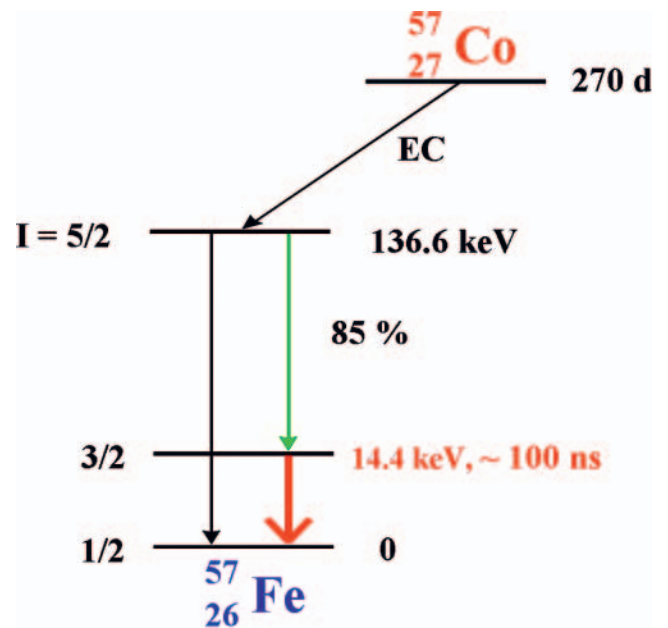
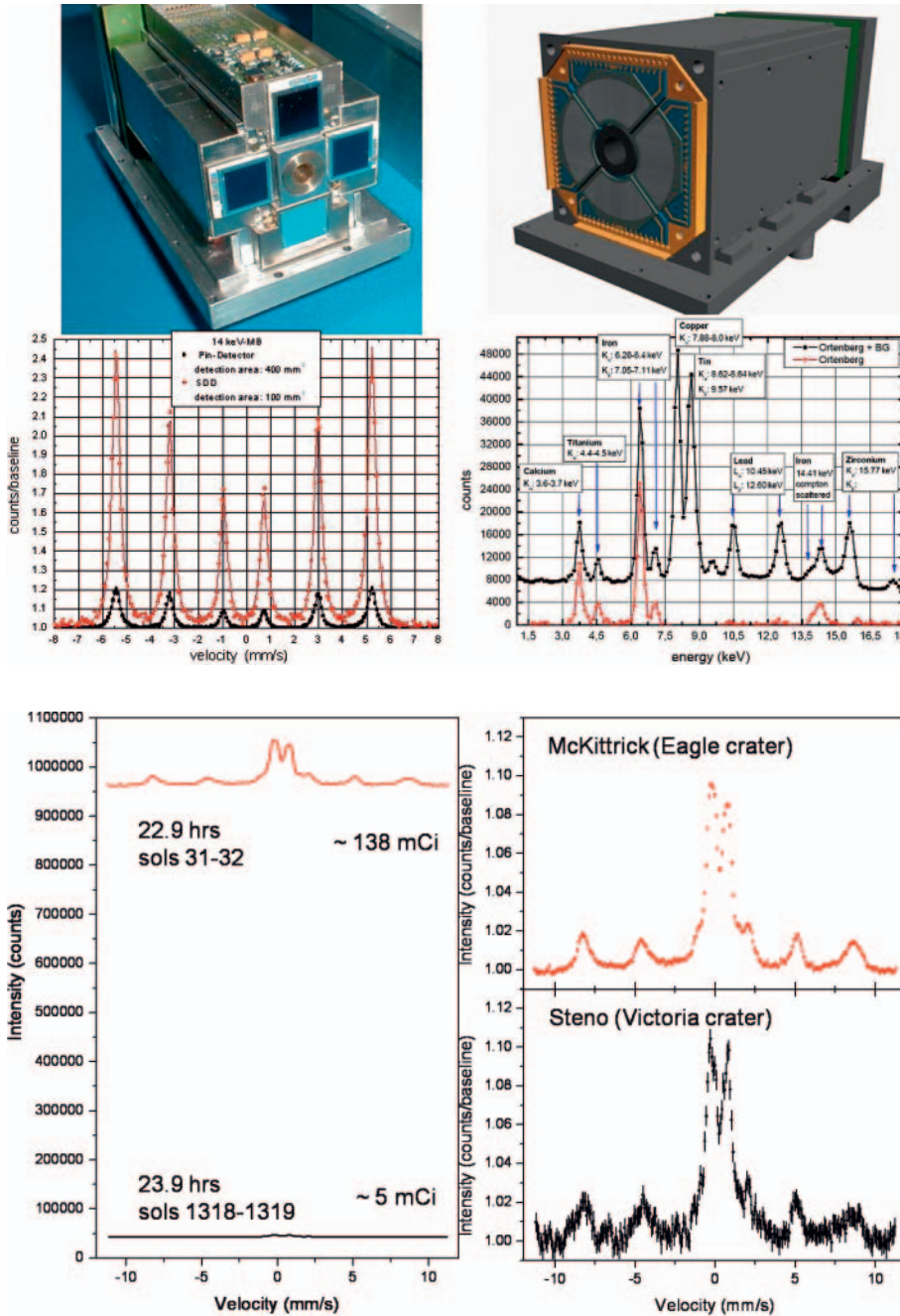


Fig. 5. A simplified decay scheme of  $^{57}\text{Co}$ , which decays via electron capture (EC) to  $^{57}\text{Fe}$ . The decay path via the first excited nuclear state of  $^{57}\text{Fe}$  with spin state  $I = 3/2$  provides the 14.4 keV  $\gamma$ -radiation necessary for the Mössbauer experiment. The half-life of the  $^{57}\text{Co}$  isotope is 270 days.



**Fig. 6.** Silicon Drift Detectors (SDD; top right) provide a higher energy resolution than Silicon PIN diodes (top left) and therefore lead to an increase in signal-to-noise ratios by approximately one order of magnitude. The Mössbauer spectrum at the lower left shows the increase of the signal although only one of four detector segments, 1/4 of the area of the four PIN diodes, was used to obtain the spectrum. SDDs also enable the simultaneous acquisition of X-Ray Fluorescence (XRF) spectra. An example of an XRF spectrum of a basalt from the Ortenberg region in Germany is shown on the lower right, before (black squares) and after (red circles) background subtraction.

**Fig. 7.** Comparison of Mössbauer spectra obtained after approximately the same measurement times but different MB source activities. The spectra were obtained on the same S-rich outcrop material dominating Meridiani Planum, the landing site of Mars Exploration Rover Opportunity. The spectrum on the target 'McKittrick' was obtained 31 sols after Opportunity's landing, the spectrum on 'Steno' on sols 1318–1319 of the mission several kilometres away. A sol is a day on Mars, which is *c.* 39 minutes longer than an Earth day. McKittrick contained 16.5 wt% FeO as total Fe, Steno 16.1 wt%. On the left hand side, the spectra are compared in absolute counts per velocity channel, on the right hand side normalised to the baseline. The vertical error bars are the square root of the counts in each velocity channel.

rendezvous with comet 67P/Churyumov-Gerasimenko in 2014 (Klingelhöfer *et al.* 2007a). SDDs provide a better energy resolution compared to the Si PIN diodes used as detectors so far,  $\sim 300$  eV compared to  $\sim 1$  keV at room temperature, leading to significantly improved signal-to-noise ratios (Fig. 6) and therefore shorter measurement times. They enable the additional acquisition of XRF spectra also for the analysis of lighter elements down to Mg. An energy spectrum is acquired and background subtracted in XRF mode, whereas the thresholds in the discriminator are kept constant during the MB experiment to only count 14.4 keV or 6.4 keV events. The  $^{57}\text{Co}$  source acts as excitation source for the X-rays with its 14.4 keV MB radiation and also its 122.2 keV and 136.6 keV emission lines (Fig. 5). Consequently, the field of view is larger in XRF mode, because the collimator was designed specifically to limit the opening angle of the 14.4 keV radiation to mitigate the effects of cosine smearing in MB spectra (cf., e.g. Klingelhöfer

*et al.* 2003), but it is less effective in the 122.2 keV and 136.6 keV energy range. By combining MB and XRF spectroscopy in a field-portable instrument, MIMOS IIa thus enables the simultaneous acquisition of elemental chemistry and Fe-bearing mineralogical data *in-situ* in a non-destructive way.

With a given detector system, the count rate and therefore the measurement time needed to obtain a MB spectrum of statistically good quality are directly proportional to the Fe content of the sample and the MB source activity. On Earth, the source activity can be maintained by replacing a source after several half-lives with a fresh source. This is not possible during space missions. Some space missions may take longer than a half-life (270 days for  $^{57}\text{Co}$ ) to even reach their destination. In addition, time allocated for individual measurements is limited during such missions. Fig. 7 illustrates such problems on the basis of the experience with the Mars Exploration Rovers. Here the unexpected, but welcome, long duration of the

mission posed a challenge. At the beginning of the mission, 22.9 hours exceeded the usually allocated 8 hours to obtain a good quality MB spectrum by far. Approximately 5 half-lives of the  $^{57}\text{Co}$  source later in the mission, a full day was closer to the minimum time necessary to obtain a MB spectrum of reasonable quality. During measurement times, the rover is immobilised. While this happened at most for a day at the beginning of the mission, it amounts to several days or even weeks in April 2010 at which time the Mars Exploration Rovers are still operational. This example shows that reduction of measurement times through increased signal-to-noise ratios resulting from the use of SDDs is a significant and paramount improvement.

## TERRESTRIAL APPLICATIONS

### Identification of air pollution sources

The identification of air pollution sources is an important goal of monitoring air quality in industrial and urban regions and helps to determine investment priorities to reduce the impact of these sources. Many urban areas monitor only the dust concentration in the air. Where on-line samplers are used, the characterization itself is often performed in the laboratory. However, because fine dust particles/particulate matter are very reactive and may be altered by changes in humidity or contact with gases such as  $\text{O}_3$  or  $\text{SO}_x$ , late characterization could render the source identification and assessment difficult; the control of a possibly problematic source will not be efficient. A better control presumes on-line and *in-situ*, ideally real-time, monitoring.

De Souza *et al.* (2000, 2001) used MB spectroscopy to identify iron-bearing materials in airborne particles and atmospheric aerosols in the Metropolitan Region of Vitória (MRV), Espírito Santo, Brazil. The MRV consists of four cities with overall nearly 1.5 million inhabitants and covers an area of 1461 km<sup>2</sup>. It houses a large industrial complex, is undergoing expansion and has to bear intense traffic. MIMOS II was installed inside an airborne particle sampler in which air was actively pumped through a particle filter. The necessary power was supplied by a 45 W battery. The instrument was mechanically insulated from vibrations caused by the pump system, which would bring noise to the MB drive. Additional shielding for the MB source was installed in the sampler. Two sampling points were selected: Ilha do Boi in Vitória city and Bela Aurora in Cariacica. The sampling points were chosen considering the predominant wind direction (Ilha do Boi, where wind blows from the industrial to the urban area; Fig. 8) and where high concentration of particulate matter have been recorded (Bela Aurora).

Hematite was identified as a predominant phase in the suspended particles from Vitória metropolitan region, Brazil. As subordinate phases goethite, pyrite, iron-containing silicates, an ultra-fine  $\text{Fe}^{3+}$  phase, and magnetite were detected. Hematite stems mostly from industrial plants producing iron ore pellets (there are seven in VMR) and from soil. MB measurements in the laboratory at liquid nitrogen temperature show no Morin transition in spectra from the soil collected in the surroundings. Goethite stems from soil and pyrite from handling and storing coal in the industrial area. Ultra-fine particles are a result of strongly weathered tropical soils and industrial emissions. Magnetite is related to steelwork plants and silicates stem from soil and civil constructions. The *in-situ* analyses have the advantage that no sample preparation is necessary, the instrument can be installed in several places (e.g. in a chimney or in a different particle size sampler). The main disadvantage of the system is that it cannot give quick results, i.e. every

minute. The use of MIMOS IIa with increased signal-to-noise ratios would significantly decrease necessary measurement times, however.

### Borehole investigation for *in-situ* monitoring of the green rust mineral fougérite

Mixed-valence green rust minerals are very reactive and play an important role as electron donors and/or acceptors in (bio)-geochemical redox cycles in hydromorphic soils on Earth; Fe is controlled by mineral – solution equilibria. The generalised formula of the green rust mineral fougérite can be written  $[\text{Fe}^{II}_{1-x}\text{Mg}_y\text{Fe}^{III}_x(\text{OH})_{2+2y}]^{x+}[\text{xA}, \text{mH}_2\text{O}]^{x-}$ , where x is the ratio  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  and A the intercalated anion (Feder *et al.* 2005). Because green rusts are very reactive, x could seasonally vary due to fluctuations in the water table. Such variations can only be measured *in-situ*.

To monitor such changes as a function of depth in the soil and with time, a MIMOS II instrument was mounted into a Plexiglas tube (Fig. 9). The Plexiglas tube was lowered into a borehole into hydromorphic soil (gleysol) at the field site in Fougères, France, permitting investigations from 15–106 cm depth with a precision of  $\pm 1$  mm. In the ‘scan’ mode, the instrument acquires up to 13 MB spectra at different depths, whereby the length of acquisition times and the depth are programmable parameters. These are sent to the instrument before starting a new session via a laptop PC. From then on all operations run autonomously without any connection to a PC necessary. No additional human interference is required after programming; the setup will work autonomously up to several weeks, only depending on the mode of power supply (Rodionov *et al.* 2006).

Feder *et al.* (2005) obtained MB spectra repeatedly exactly at the same points at different times to follow mineralogical transformations with time. Fougérite is the only iron mineral identified, except in summer when lepidocrocite is present in addition to fougérite. The x-ratio in fougérite deduced from MB spectra of the upper part of the studied soil profile is approximately 2/3 ( $\text{Fe}^{II}\text{Fe}^{III}_2(\text{OH})_8$ ), in the horizons showing oximorphic properties. The x-ratio is only 1/3 in the deepest horizons that show reductomorphic properties ( $\text{Fe}^{II}_2\text{Fe}^{III}(\text{OH})_7$ ). Fast mineralogical transformations were observed at well-defined points in soil, as evidenced by x-ratio variations observed when MB spectra were acquired at different times at the same depth. Variations of the level of the water table and of pe and pH of the soil solution were simultaneously observed and could explain these mineralogical transformations. The following mineralogical transformations appear to occur seasonally: Under aerobic conditions as a result of low water tables in the driest periods of summer, fougérite is completely oxidised to  $\text{Fe(III)}$  oxyhydroxides (lepidocrocite). Fresh organic matter supply and water saturation in autumn turn the milieu anoxic. Lepidocrocite is reduced and dissolves, releasing  $\text{Fe}^{2+}$  into solution. The soil colour changes from ochre to blue. Air-saturated rainfall replenishes dissolved oxygen and oxidizes  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , which coprecipitates with  $\text{Fe}^{2+}$  to form fougérite with variable x-ratios as a result of alternating anoxic and oxic periods. Eventually, during the next summer when the water table falls and air enters the soil profile, fougérite transforms back by complete oxidation into lepidocrocite.

### Rio Tinto field investigations

The investigation of terrestrial Mars analogue sites is essential to interpret observations made on Mars. With its sulphate-rich mineralogy, the Rio Tinto in southwestern Spain is recognised



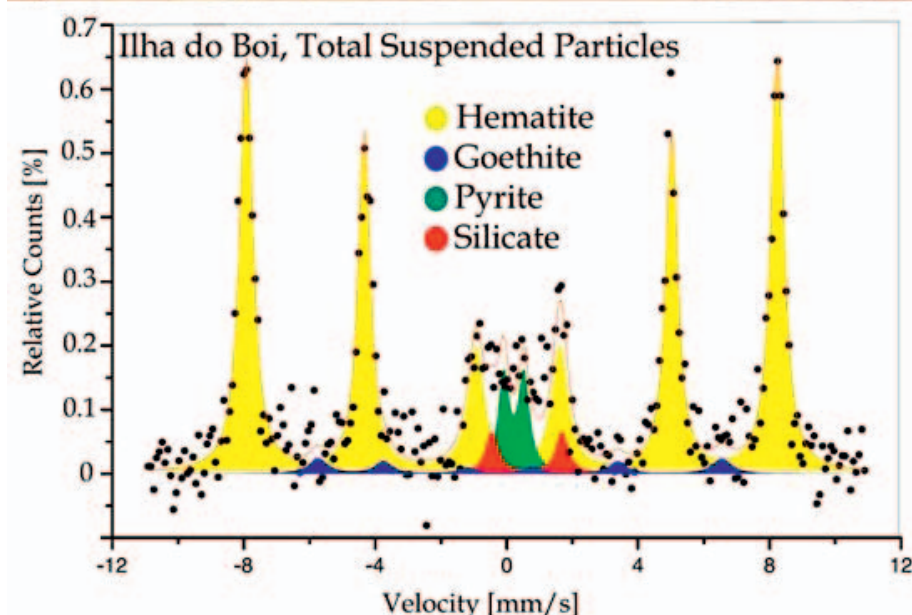


Fig. 8. Air pollution samplers located at Ilha do Boi, Vitória, Brazil and a Mössbauer spectrum obtained with a MIMOS II instrument in a sampler. Figure modified from de Souza (2004).

as an analogue site for Meridiani Planum, the landing site of the Mars Exploration Rover Opportunity (e.g. Squires *et al.* 2006). The Rio Tinto exhibits a near constant acidic pH of *c.* 2.3 along its 100 km course. The water of the river is rich in iron and accommodates a diverse community of extremophilic microbes.

Mineralogical studies with MIMOS II in connection with a portable Raman spectrometer (Rull *et al.* 2008) and the portable “Terra” XRD/XRF instrument (Blake *et al.* 2009) were performed during two field trips in 2008 and 2009 (Fleischer *et al.* 2010). Close to the stream margin, seasonal deposits of efflorescent precipitates and evaporite crusts can be observed. The MIMOS II instrument deployed at a Rio Tinto sampling site and an example of evaporitic deposits are shown in Fig. 10. These evaporite minerals may easily be altered by a change of their environment (e.g., temperature and humidity). Thus, representative samples were analysed *in-situ*. Light-yellow and white, thin crusts and ‘popcorn-texture’ evaporites were found to contain a mixture of the ferric sulphates copiapite ( $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_4(\text{SO}_4)(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ ) and coquimbite ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ). The ferrous sulphates melanterite ( $\text{Fe}^{\text{II}}(\text{SO}_4)$

$\cdot 7(\text{H}_2\text{O})$ ) and rozenite ( $\text{Fe}^{\text{II}}(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$ ) were detected in loose crusts exhibiting shades of green and blue. Layered sulphates could only be measured *in-situ*. Measurements obtained on a red crust on top of dark river bedrock revealed the presence of jarosite in the crust and pyrite in the substrate. An additional, thin, white or yellow crust was covering the red crust at some places (Fig. 10). Jarosite from the red crust and copiapite with coquimbite from the light crust were clearly detected. Both spectra are shown in Fig. 11. In the spectra, subspectral areas reflect the thicknesses of the layers and different Fe contents of their components. MIMOS II was the only instrument able to detect goethite of low crystallinity in association with jarosite in an orange-coloured deposit.

#### Archaeometry/art preservation

Studies of ancient ceramics became the first instance of the use of MB spectroscopy in what one commonly calls archaeometry: the application of scientific methods in studies of archaeological sites and artefacts. Changes which pottery clays undergo during firing are reflected in the MB spectra of the fired



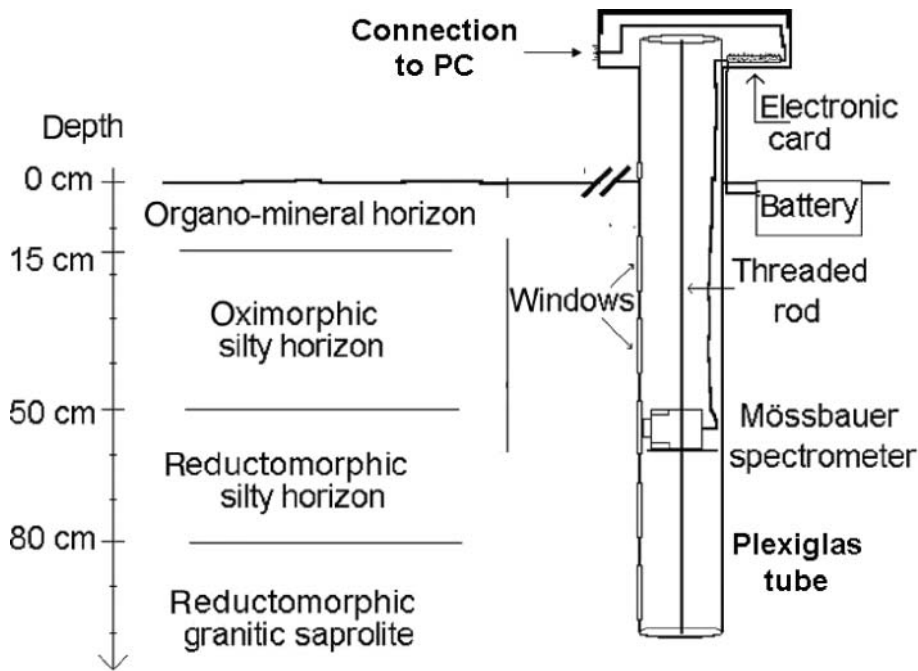


Fig. 9. Schematic drawing of the Mössbauer borehole investigation setup to study the seasonal variation of oxidation states in the mixed-valence green rust mineral *fougerite* in the field (figure modified from Feder *et al.* 2005).



Fig. 10. The MIMOS II sensor head measuring an evaporite sample at Rio Tinto (above). Efflorescent precipitates (image centre), thin light-coloured crust and red-coloured crust covering the river bed-rock (below). See online version for colour.

ceramics and hence can be used, even after millennia of burial, to gain information on the original firing conditions and thus on the techniques. Other areas of archaeological interest are, for example, corrosion of steel or properties in iron artefacts,

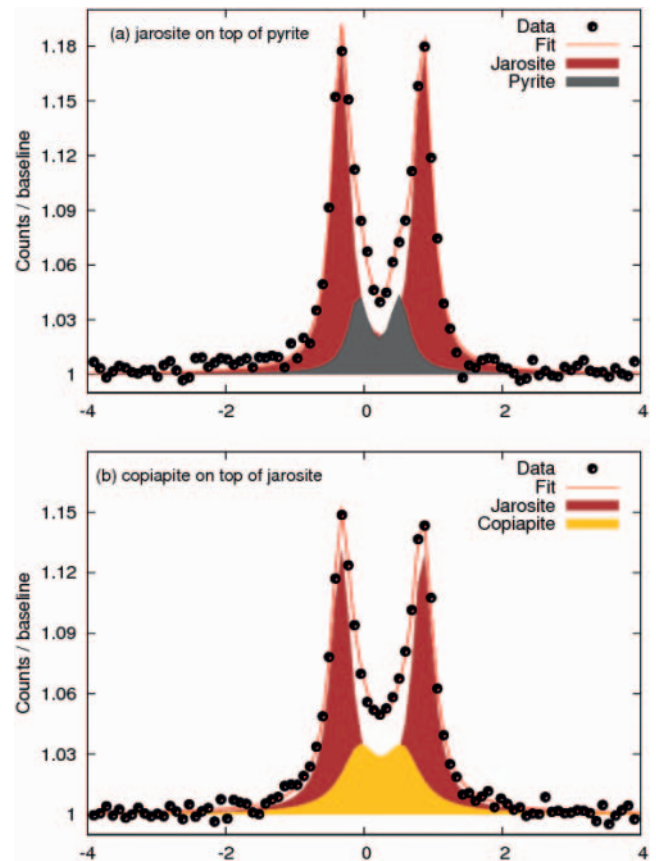
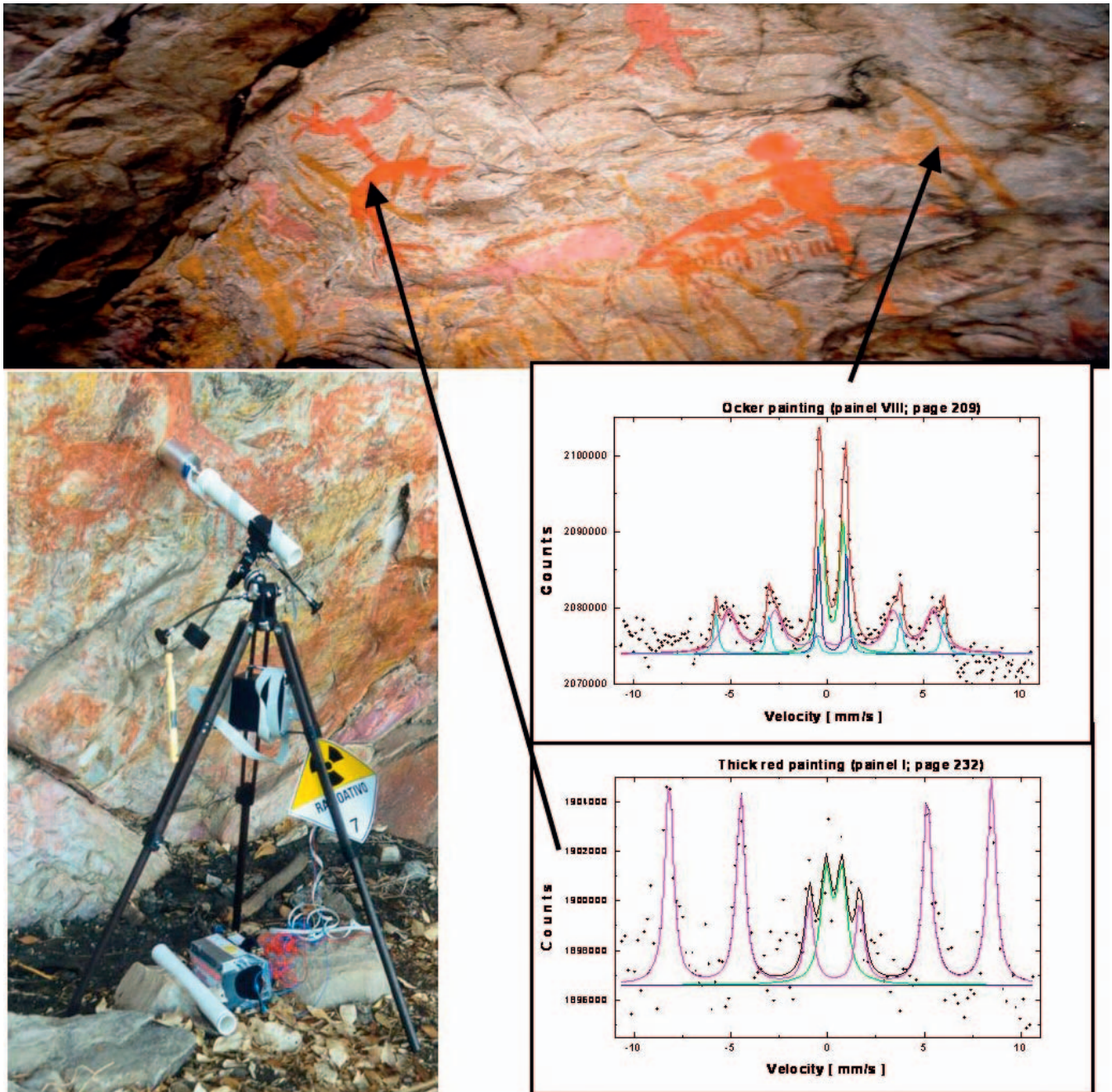


Fig. 11. Mössbauer spectra obtained *in-situ* on layers of precipitated minerals.

slags from prehistoric copper, tin and iron production, and pigments and paintings (e.g. Wagner & Kyek 2004, and references therein). An instrument like MIMOS IIa opens up several new dimensions: (1) non-destructive analyses of unique archaeological artefacts or works of art; (2) the additional



**Fig. 12.** Non-destructive analysis with MIMOS of ancient rock painting in Brazil (near Belo Horizonte, Minas Gerais). MIMOS is mounted on a support and touches the painting on the wall for measurement. Two spectra were recorded, one of red paint, the other of an ochre paint. Mössbauer spectroscopy distinguishes between different iron oxide pigments. See online version for colour.

capability to obtain XRF elemental analyses; and (3) the portability enables taking the instrument to the artefact or work of art, may it be in a museum or, for example, at an archaeological excavation site, because it is inherently risky to move art objects (Chiari 2008): insurance companies charge high fees to cover damage during transportation, often prohibiting the movement of an object for study, and some items are simply not transportable.

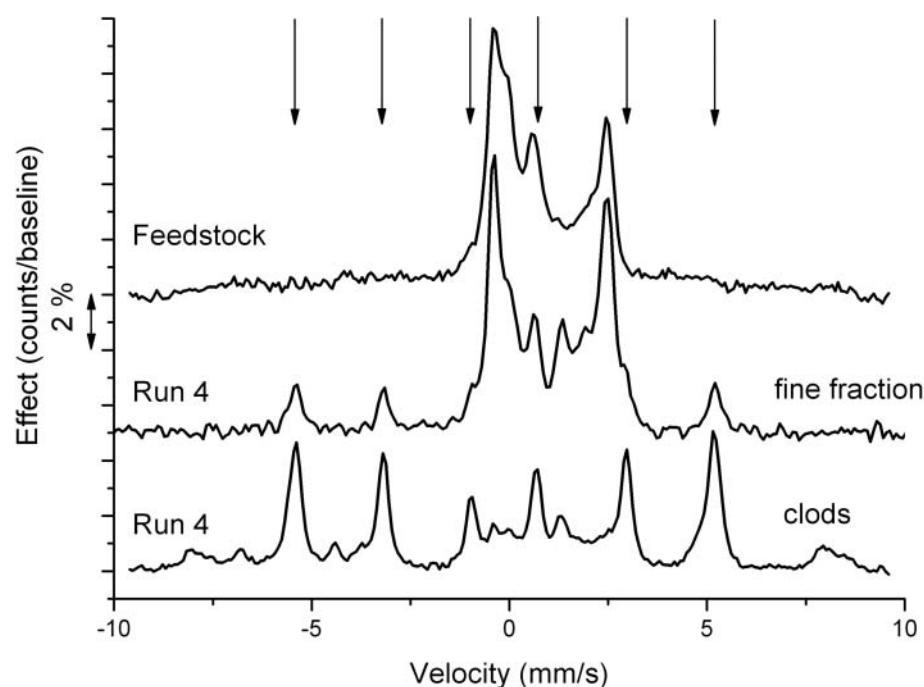
Several prehistoric rock paintings are found at the archaeological site of Santana do Riacho, 90 km NE of Belo Horizonte in Minas Gerais, Brazil. To investigate the nature of the pigment used in the predominantly red and yellow paintings, a MIMOS instrument was taken to the site, mounted on a tripod and brought in contact with the paintings on the wall for

measurement (Fig. 12; Klingelhöfer *et al.* 2002). MB spectra reveal that hematite is the Fe-bearing pigment in the red colours (Fig. 12) and goethite is the Fe-bearing pigment in the yellow colours. Ochre colours show a more complicated pattern in MB spectra (Fig. 12), and represent a mixture of goethite with other Fe-bearing phases.

#### *Lunar in-situ resource utilization*

NASA and international partners are planning a human return to the Moon. Essential consumables like oxygen must be produced from materials on the lunar surface to enable a sustained, long-term presence of humans on the Moon. Oxygen can be produced from the lunar regolith by hydrogen reduction





**Fig. 13.** Mössbauer spectra of the feedstock and two processes samples in a regolith reduction plant. The positions on the velocity scale of the Fe<sup>0</sup> lines are indicated by arrows. The reduction in the clods is significantly enhanced when compared to the fine fraction, which was extracted earlier from the reaction chamber than the clods. This indicates non-uniform temperatures within the reaction chamber either spatially or in time.

of metal cations (primarily Fe<sup>2+</sup> as FeO in minerals) to metal (Fe<sup>0</sup>) with the production of water. The hydrogen source is residual hydrogen in the fuel tanks of lunar landers. Electrolysis of the water produces oxygen and hydrogen. Oxygen can be consumed, hydrogen is recycled. Experiments by Allen *et al.* (1994, 1996) have shown that oxygen yield is proportional to the iron content of the regolith, and that the temperature during the reduction process plays a significant role. Ilmenite and glass, for example, are reduced at temperatures of 900°C. Olivine is converted to pyroxene by reduction of its Fe<sup>2+</sup> and release of oxygen at 1000°C and higher. At 1100°C, essentially all of the Fe<sup>2+</sup> is reduced to metallic iron. MB spectroscopy can aid this process in several ways: (1) oxygen yield can be calculated by quantitative MB measurements of Fe distribution among oxidation states in the regolith before and after hydrogen reduction; (2) mounted on a rover, for example, MB spectrometers can be used as prospecting tools to select the optimum feedstock for the oxygen production plants. This would be optimised when combined with XRF elemental analysis as realised in MIMOS IIa, looking for high total Fe content and easily reduced phases; and (3) the optimum temperature for the reduction process can be estimated from MB characterization of mineral phases in the selected feedstock regolith. In return, temperature inside the hydrogen reduction plants can be reconstructed from measurements on the processed material.

These applications were demonstrated with a MIMOS II instrument during the NASA Outpost Precursor for ISRU and Modular Architecture (OPTIMA) field test on Mauna Kea, Hawaii, in 2008. OPTIMA was designed to test the implementation of several hardware concepts to extract oxygen from the lunar regolith. A MIMOS II setup at the field site was used to analyze the feedstock and the processed material. Figure 13 shows MB spectra obtained from material of the same run in one of the oxygen production plants, but collected at different stages. The significantly enhanced reduction in the clods when compared to the fine fraction, which was extracted earlier from the reaction chamber than the clods, indicates non-uniform temperatures within the reaction chamber either spatially or in time. A MIMOS II instrument was also mounted on the Cratos

rover (NASA Glenn Research Center, Cleveland, OH), which is one of several rover concepts designed to excavate and transfer regolith to the stationary hydrogen reduction plants (Fig. 14).

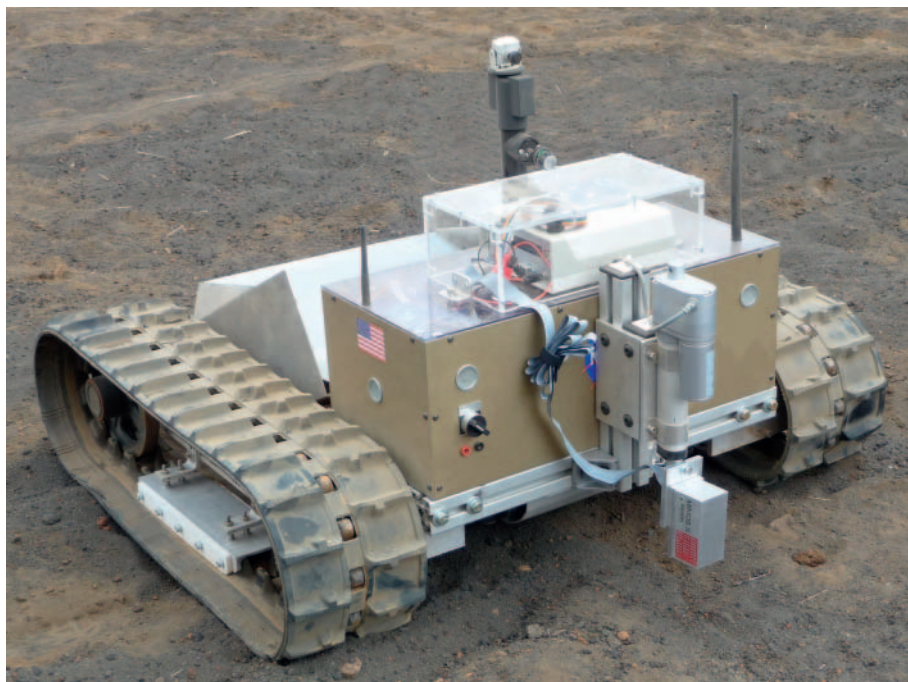
## MARS EXPLORATION

Conditions on the surface of Mars are cold and dry today but many features suggest a warmer and wetter past, at a time when life arose on Earth. The search for extinct or extant life is a major driving factor of international Mars exploration efforts. A 'Follow-the-Water' strategy has been adopted because on Earth water is the most important prerequisite for life. The primary objective of the MER mission is to explore two sites on Mars where water may once have been present, and to assess past environmental conditions at those sites and their suitability for life (Squyres *et al.* 2003). The Red Planet owes its colour to Fe-oxides, and surface materials on Mars are enriched in Fe relative to Earth. The distribution of Fe between Fe-bearing minerals and its oxidation states determined with MB spectroscopy constrains the primary rock type (e.g. olivine-bearing v. non-olivine-bearing basalt), the redox conditions under which primary minerals crystallised (e.g. presence or absence of magnetite), the extent of alteration and weathering (e.g. value of Fe<sup>3+</sup>/Fe<sub>Total</sub>), the type of alteration and weathering products (e.g. oxides v. sulphates v. phyllosilicates), and the processes and environmental conditions for alteration and weathering (e.g. neutral v. acid-chloride v. acid-sulphate aqueous process under ambient or hydrothermal conditions), thus making important contributions towards the MER mission goals (e.g. Morris *et al.* 2004; Schröder *et al.* 2004).

### Rock and soil classification and geological mapping

The two Mars Exploration Rovers, Spirit and Opportunity, are robotic field geologists equipped with the Athena Science Payload (Squyres *et al.* 2003) consisting of a 0.27 mrad/pixel, multiple filter visible to near-infrared (400–1010 nm) Panoramic camera (Pancam) and a Mini-Thermal Emission Spectrometer (Mini-TES) covering the 5–29 µm wavelength





**Fig. 14.** A MIMOS II instrument mounted on the Cratos rover (NASA Glenn Research Center) to demonstrate its capabilities as a prospecting tool. Cratos is one of several hardware concepts designed to excavate and transfer regolith to the stationary hydrogen reduction plants. The MIMOS II sensorhead is pointing downwards in the lower right of the image. The electronics box can be seen in the Plexiglas housing on top of the rover. Communications with a notebook computer were established via a wireless Bluetooth device to allow for autonomous rover operations.

region for remote sensing, and four instruments on a robotic arm for *in-situ* investigations: A Rock Abrasion Tool (RAT) to remove surface contamination and weathering rinds from rock surfaces, a 30  $\mu\text{m}/\text{pixel}$  Microscopic Imager (MI), an Alpha Particle X-ray Spectrometer (APXS) for elemental composition (Rieder *et al.* 2003), and a Mössbauer (MB) spectrometer for determining mineralogy of iron-bearing phases (Klingelhöfer *et al.* 2003).

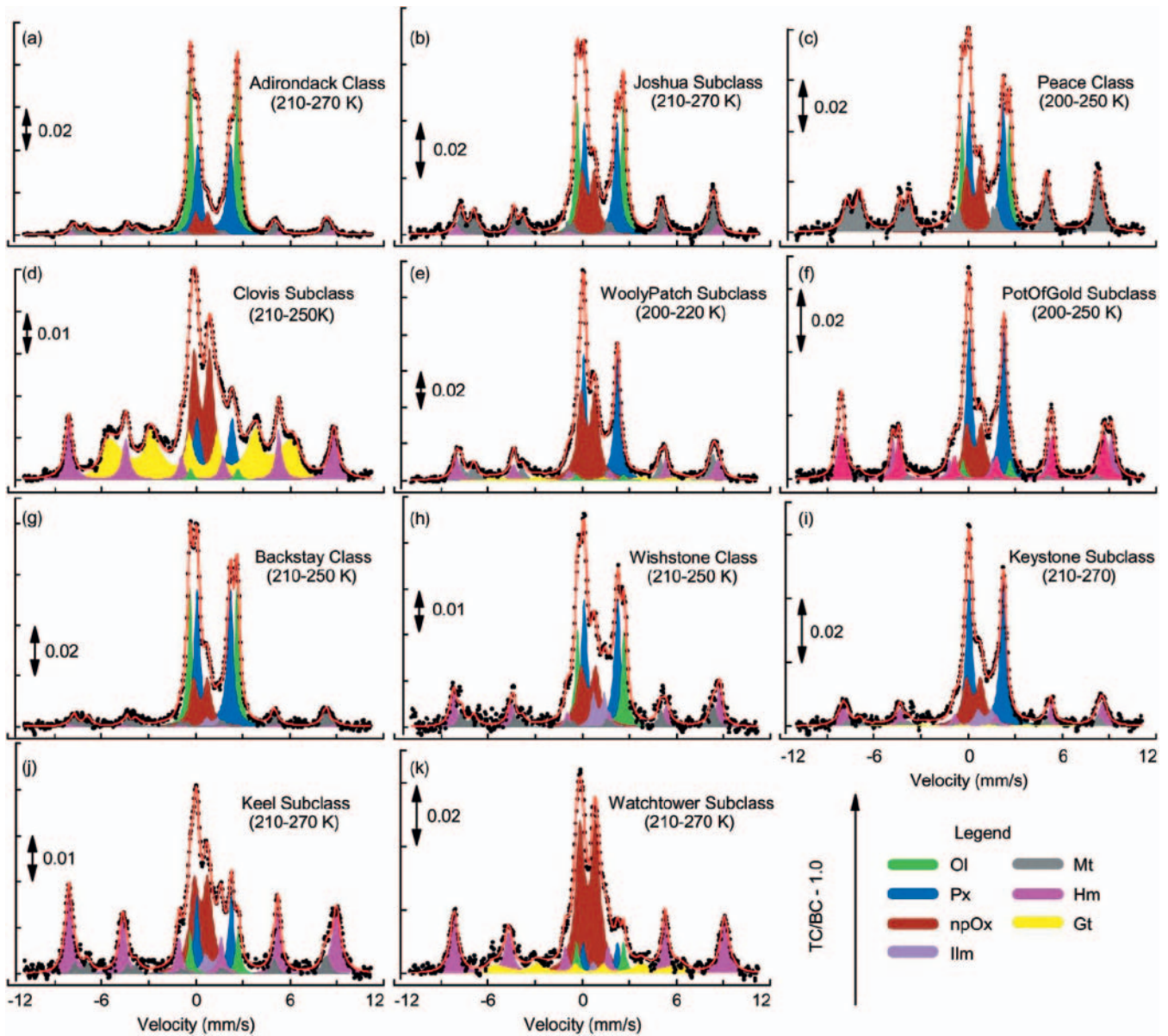
Along their traverse, the rovers investigated a wide variety of different rock and soil types, ranging from weakly altered to pervasively altered igneous rocks to layered evaporate outcrop rocks, for example. Note that we use the term ‘soil’ rather than ‘regolith’ to denote any loose unconsolidated materials that can be distinguished from rocks, bedrock, or strongly cohesive sediments. No implication of the presence or absence of organic matter is intended (cf. Banin *et al.* 1992; Banin 2005). Rocks and soils were divided into classes on the basis of their chemical composition measured with the APXS and into subclasses on the basis of their Fe-bearing mineralogical composition and  $\text{Fe}^{3+}/\text{Fe}_{\text{Total}}$  ratios determined with the MB spectrometers (Fig. 15; Ming *et al.* 2006, 2008; Morris *et al.* 2006a, 2006b, 2008).

Often, two rocks with the same chemical composition differ significantly in their Fe-bearing mineralogical composition and in  $\text{Fe}^{3+}/\text{Fe}_{\text{Total}}$  ratios as a result of isochemical alteration. Many Fe-bearing minerals can be identified on the basis of their MB parameters alone. However, in the case of non-unique MB parameter sets or complicated MB spectra, the absence or presence of certain elements helps to exclude from or to suggest inclusion of mineralogical phases into the model to fit MB spectra. In turn, the quantitative distribution of Fe between its oxidation states and between Fe-bearing mineral phases constrains the calculation of Fe-free minerals from the remaining elements.

The APXS and MB *in-situ* measurements can be reconciled with Mini-TES (McSween *et al.* 2008) and Pancam (Farrand *et al.* 2008) datasets, and thus provide ground truth for remote sensing and orbital investigations, which in turn allow placing the *in-situ* measurements into a wider geological context. During Spirit’s traverse through the Columbia Hills in Gusev Crater,

surface observations from the rover perspective of local chemical, mineralogical, and lithologic variations within generalized terrain units that are mappable in orbital Mars Reconnaissance Orbiter (MRO) High-Resolution Imaging Science Experiment (HiRISE) data were used to define more widespread Columbia Hills geological material units based on a comparison of HiRISE image characteristics of the defined material units. This exercise constitutes the first field reconnaissance geological mapping on another planetary surface (Crumpler *et al.* 2009).

The investigation of a feature in the Columbia Hills, informally named Home Plate, gives an example of how APXS and MB *in-situ* data are placed in the context of remote sensing and orbital information. Home Plate is a layered, light-toned roughly circular plateau *c.* 90 m in diameter and 2–3 m high within the Inner Basin of the Columbia Hills. Textural and geochemical observations indicate that Home Plate is the result of a hydrovolcanic explosion in which magma came into contact with subsurface fluid or ice and subsequent deposition of pyroclastic material (Squyres *et al.* 2007). Observations of Home Plate from orbit and with Pancam from Spirit’s earlier position on the summit of Husband Hill reveal clear differences in visible/near-infrared (VNIR) colours between its eastern and western regions (Schmidt *et al.* 2009). MB observations on several spots in the eastern and western regions and in between show these differences reflect changes in the mineralogical composition: spectra from the eastern side are dominated by pyroxene and magnetite and have little or no olivine whereas spectra from the western side are dominated by nanophase ferric oxides (npOx) and have significant amounts of olivine (Fig. 16; Schröder *et al.* 2008a). The npOx probably represents superparamagnetic Fe oxides. The martian diurnal temperature changes did not fall below any diagnostic blocking temperatures, nor did the chemical composition help to constrain the specific mineral. Going from east to west, the simultaneous increase of npOx, most likely an alteration phase, and olivine, one of the minerals most susceptible to aqueous alteration, presents an apparent contradiction. A basaltic glass-like signature is more apparent in Mini-TES spectra of the western side than the eastern side, but there is no indication for a glass phase in MB spectra. In contrast to the mineralogical differences,



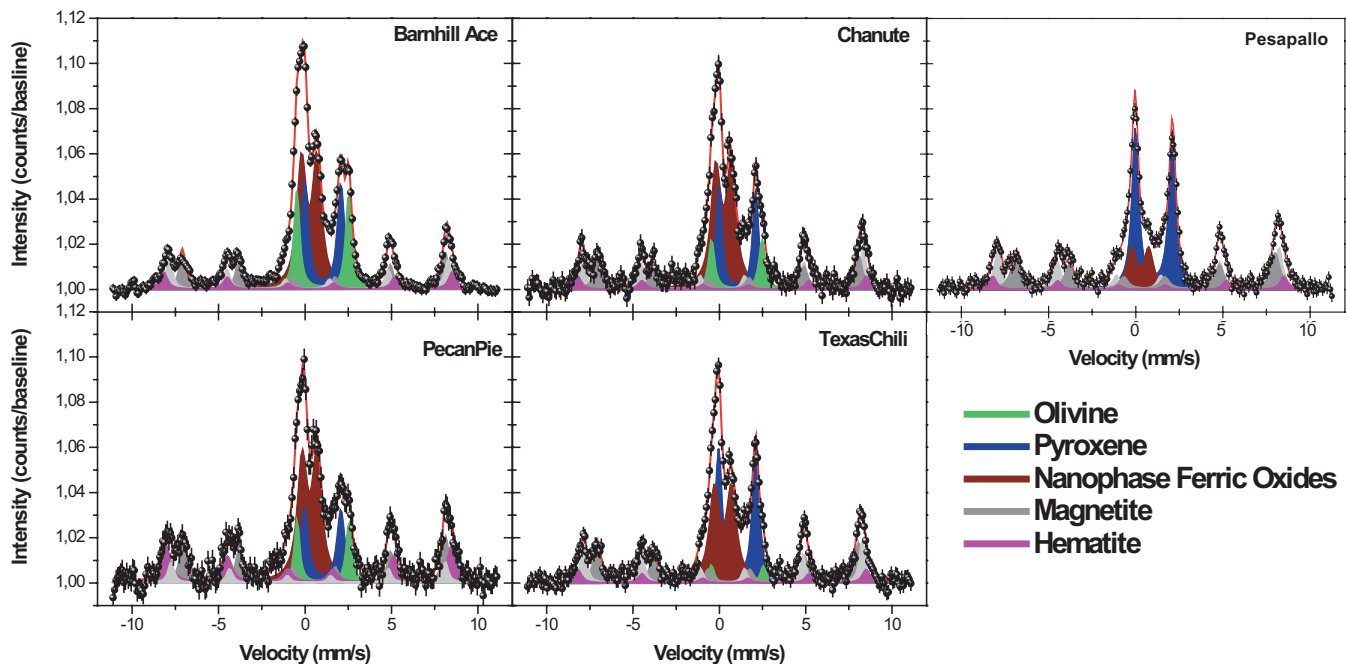
**Fig. 15.** Representative Mössbauer spectra of rock classes identified by Spirit in Gusev Crater. Clovis Class contains Clovis subclass and WoollyPatch subclass; Watchtower class contains Keystone Subclass, Keel Subclass and Watchtower Subclass; PotOfGold Subclass and Joshua Subclass were not classified based on elemental composition because clean surfaces of these rocks were not available for analysis with the APXS (Ol, olivine; Px, pyroxene; npOx, nanophase ferric oxides; Ilm, ilmenite; Mt, magnetite; Hm, hematite; Gt, goethite; Figure adapted from Morris *et al.* 2006a).

compositional similarities in major elements along with geological observations (Lewis *et al.* 2008) indicate that the upper, cross-bedded materials of Home Plate belong to the same stratigraphic unit. However, APXS observations in several locations reveal systematic differences. Eastern Home Plate has higher Si/Mg, Al, Zn, Ni, and K, while Cl and Br are higher in the west. Schmidt *et al.* (2009) propose overprinting by both high and low temperature alteration as a possible explanation to resolve these discrepancies. Olivine and basaltic glass reflect the primary igneous mineralogy of Home Plate rocks. High temperature alteration in the eastern regions led to the recrystallization of olivine into pyroxene and magnetite, and the glass may have devitrified with the Fe-bearing component forming magnetite. Low temperature alteration in the western region may have lead to devitrified glass with the Fe-bearing component forming npOx.

### Habitability/astrobiological implications

Liquid water is the most important prerequisite for life on Earth and motivates the search for signatures of aqueous activity in the past or at present on Mars. Olivine identified in dust and soil by both Spirit's and Opportunity's MB spectrometers suggests that physical rather than chemical weathering processes dominate on contemporary Mars (Morris *et al.* 2004), and the apparent global distribution of olivine-bearing dust and soil (Yen *et al.* 2005) reflects the overall extremely arid conditions on Mars. By contrast, aqueous minerals identified in outcrop rocks such as the Fe oxyhydroxide goethite ( $\alpha$ -FeOOH) in the Columbia Hills in Gusev crater (Morris *et al.* 2006a) or the Fe hydroxide sulphate jarosite in layered evaporate outcrop rocks at Meridiani Planum (Klingelhoefer *et al.* 2004) provide evidence for wet conditions in the past.





**Fig. 16.** Mössbauer spectra of representative targets from five different locations on Home Plate. Rows correspond to relative latitude, columns correspond to approximate relative longitude. Barnhill Ace and Pecan Pie were measured on the western side of Home Plate, Pesapello on the eastern side, and Chanute and Texas Chilli were on the northern and southern ends of Home Plate, respectively.

Jarosite is a ferric sulphate hydroxide whose generalised formula can be written  $(K,Na,H_3O)(Fe_{3-x}Al_x)(SO_4)_2(OH)_6$ , where  $x < 1$ . The end members  $KFe_3(SO_4)_2(OH)_6$ ,  $NaFe_3(SO_4)_2(OH)_6$ , and  $(H_3O)Fe_3(SO_4)_2(OH)_6$  are jarosite, natro-jarosite, and hydronium jarosite, respectively. For jarosites, the MB quadrupole splitting parameter,  $\Delta E_Q$ , increases in the order  $K > Na > H_3O$  and with  $Al^{3+}$  substitution for  $Fe^{3+}$ . The  $\Delta E_Q$  for martian jarosite is most consistent with  $(K,Na)(Fe,Al)_3(SO_4)_2(OH)_6$  that is  $Na^+$ - or  $K^+$ -rich jarosite with possible Al substitution (Klingelhöfer *et al.* 2004; Morris *et al.* 2006b).

Jarosite is a mineralogical marker for aqueous processes because it contains the equivalent of *c.* 10 wt.%  $H_2O$  in its structure as the OH anion. The average S-rich outcrop rock at Meridiani Planum has the equivalent of *c.* 2%  $H_2O$  associated with jarosite alone. An important aspect of the jarosite detection is that acidic conditions ( $pH < 4$  at room temperature) are required for its formation. The alteration of basaltic precursor material under oxidizing, acid-sulphate conditions to form jarosite and other phases in the S-rich outcrop rocks at Meridiani Planum could have occurred under conditions provided, for example, by interactions with acid-sulphate, possibly hydrothermal waters and/or condensation of  $SO_2$ -rich volcanic emanations (Morris *et al.* 2006b). The past environmental conditions characterised by low pH inferred from the detection of jarosite at Meridiani Planum have implications for the suitability for life at Meridiani Planum. While microbial populations on Earth have adapted to low pH levels, they would have challenged prebiotic chemical reactions thought to have played a role in the origin of life on Earth (Knoll *et al.* 2005).

The identification of sulphates as well as ferrous and ferric substances connected to aqueous activity by MB has astrobiological implications (Schröder *et al.* 2006a) because redox cycling of Fe and the reduction of S provide energy for microbial metabolism under anaerobic conditions on Earth. A less Earth-centric (i.e. carbon-based life dependent on the availability of liquid water) approach to the search for extra-terrestrial life, the ‘Follow-the-Energy’ approach, has been suggested by Hoehler *et al.* (2007).

### Meteorites on Mars

Several loose rock fragments investigated by Opportunity had an unusual elemental composition compared to other known martian rocks. The MB detection of Fe metal and troilite in these rocks confirm their identification as stony meteorites (Fig. 17; Schröder *et al.* 2006b, 2008b, 2010). These stony meteorite fragments all have a remarkably similar chemical and mineralogical composition. In elemental ratio plots (Fig. 18; Schröder *et al.* 2008b) they plot close to the howardite, eucrite and diogenite achondrite groups, but have enhanced amounts of Fe and Ni, which led to a possible classification as mesosiderites (Schröder *et al.* 2006b). Because mesosiderites are a relatively rare group of meteorites, and because of their similarity in chemical and mineralogical composition these meteorites are probably paired, i.e. fragments of the same originally larger body. The individual meteorite fragments were found kilometres apart to the north and south of Victoria crater, which was extensively studied by Opportunity (Squyres *et al.* 2009) because its crater walls reveal more than 10 m of stratigraphy of the S-rich layered outcrop rocks defining Meridiani Planum. The largest observed accumulation of the meteorite fragments occurs at its rim, based on Pancam and Mini-TES remote sensing results. It is possible that these fragments are part of the impactor that created Victoria (Schröder *et al.* 2010).

Mars is one of the few planetary bodies in the solar system allowing for human exploration and possible extended stays of human explorers. Inventive ways for *in-situ* resource utilization are needed to enable such an endeavour. Compared to the Moon, meteorites have a greater chance to survive impact on Mars because of its atmosphere. Compared to Earth, the current extremely arid climate on Mars lets meteorites persist for much longer times and thus accumulate. Landis (2009) suggested that iron meteorites may be collected to provide steel as a construction resource on Mars for future human exploration. Several iron meteorites have been discovered by the Mars Exploration Rovers, most notably ‘Meridiani Planum’, which was named after the location of its find. Meridiani Planum is a



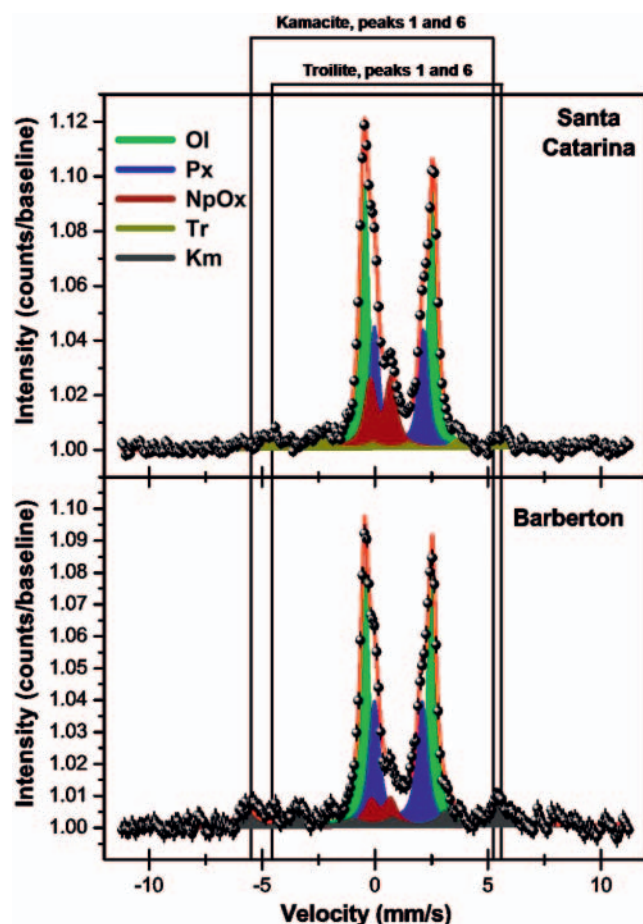


Fig. 17. Mössbauer spectra of (top) Santa Catarina and (bottom) Barberton. Peaks 1 and 6 of the magnetically split sextets typical for kamacite and troilite are indicated. Troilite in Barberton and kamacite in Santa Catarina are, if present, hard to resolve against the statistical background. Ol, olivine; Px, pyroxene; NpOx, nanophase ferric oxides; Tr, troilite; Km, kamacite (Figure adapted from Schröder *et al.* 2008b).

IAB iron meteorite and the first officially recognised meteorite on the surface of another planet (Schröder *et al.* 2008b).

## INTO THE BEYOND – FUTURE ASTEROID MISSIONS

Asteroids are the parent bodies of most known meteorite groups. The identification and grouping of meteorites on the surface of Mars with the help of XRF and MB spectroscopy (Schröder *et al.* 2008b) demonstrate the value of a combination of these techniques, as realised in MIMOS IIa, for landed asteroid missions. Mars' moon Phobos may be a gravitationally captured asteroid. The Russian Phobos-Grunt mission will attempt to return samples from its surface to Earth. The mission was originally scheduled to launch in October 2009 but has been postponed to 2011. A MIMOS II instrument without an XRF channel has already been delivered as payload element for the lander module (Klingelhöfer *et al.* 2007b). ASTEX is a feasibility study of an *in-situ* exploration mission to two near-Earth asteroids (NEAs), one of primitive nature and one a fragment of a differentiated asteroid, funded by the German Space Agency DLR. The mission scenario consists of an orbiting and landing phase at each target. A MB spectrometer has been suggested for the lander payload (Nathues *et al.* 2008). MARCO POLO is a joint European–Japanese sample return

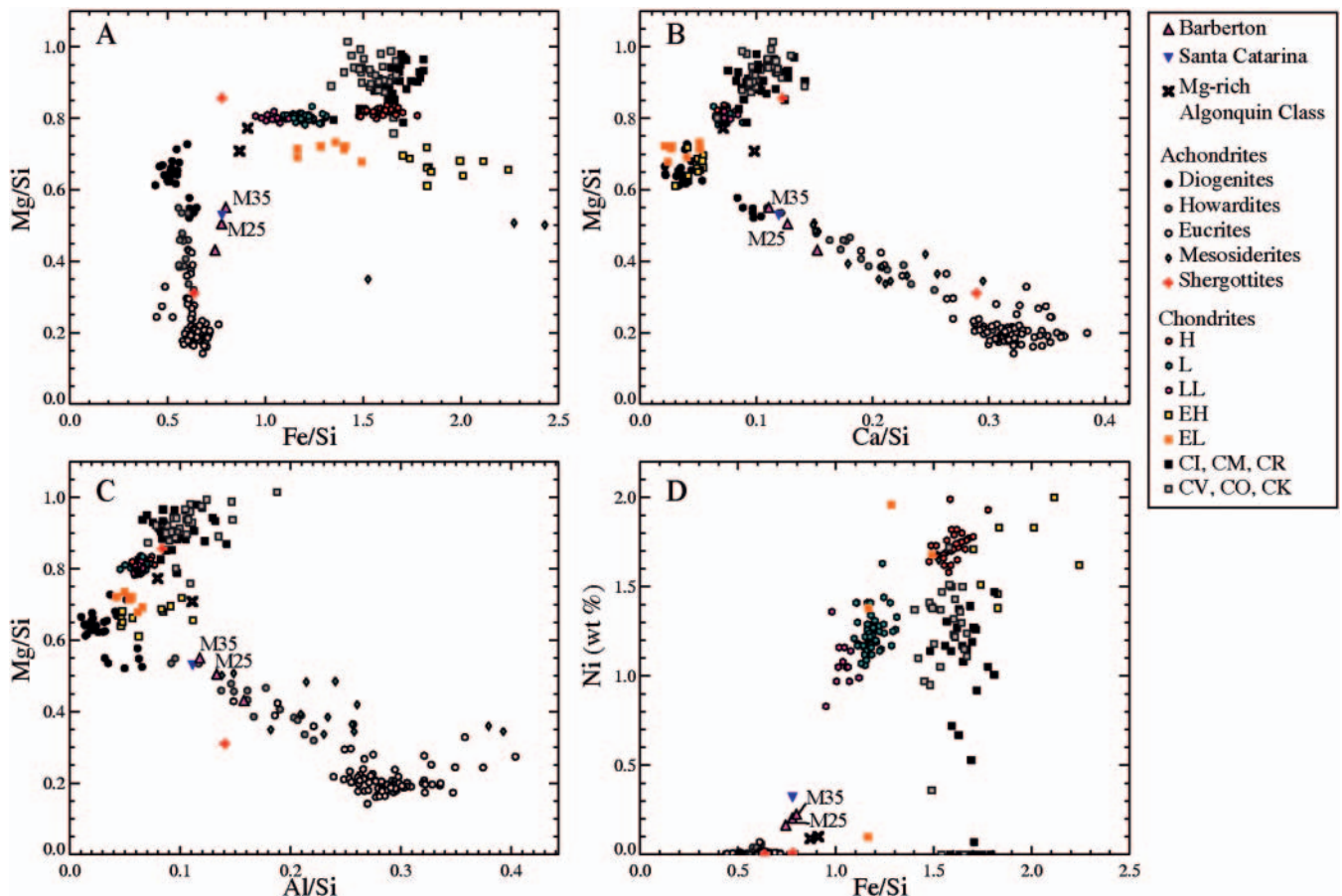
mission to a Near-Earth Object (Barucci *et al.* 2009). An APXS is among the payload suggested for an optional lander. A better knowledge of the chemical, mineralogical and structural makeup of asteroids and near-Earth asteroids in particular is important for the understanding of the origin and evolution of our Solar System, their potential for mining and ISRU, and the development of Earth impact mitigation strategies. Robotic precursor missions are an important step to future human exploration of asteroids (Landis *et al.* 2009).

## SUMMARY AND OUTLOOK

The element Fe occurs naturally as  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and, to a lesser extent, as  $\text{Fe}^0$ . Many fundamental (bio)geochemical processes are based on redox cycling between these oxidation states. Mössbauer spectroscopy is a powerful tool to study Fe-bearing substances. Miniaturised MB spectrometers (MIMOS II) were developed for NASA's Mars Exploration Rovers, designed as robotic field geologists. Since landing in 2004, these instruments have determined the Fe-bearing mineralogy and Fe oxidation states of rocks and soils on Mars. These data, for example, enabled the classification of rocks and soils and subsequently provided ground truth for geological mapping. MB spectra traced alteration gradients across geological features such as Home Plate and provided ground truth for geological mapping. The identification of the Fe hydroxide sulphate jarosite, for example, provided evidence for aqueous processes and constraints on habitability because this mineral forms only at low pH. The MER MB spectrometers were also instrumental in identifying extra-martian materials, i.e. meteorites on Mars.

The MIMOS instrument is field-portable and its setup in backscattering geometry allows non-destructive *in-situ* measurements. We have shown numerous examples of the resulting diverse applicability. Terrestrial applications include the on-line identification of air pollution sources in Brazil; seasonal changes of the mixed-valence green rust mineral fougérite as a function of soil depth and seasonal changes in the water table; the *in-situ* study of hydrated sulphates which form seasonally at Rio Tinto in Spain; or taking the instrument into the field for a non-destructive analysis of the pigments used in prehistoric rock paintings. Oxygen can be extracted from the lunar regolith for ISRU purposes of future manned missions to the Moon. Because oxygen yield primarily depends on the FeO content of the regolith, MB spectroscopy can be used as a process monitor and prospecting tool, which we have demonstrated with MIMOS II in a field test on Hawaii. Several landed asteroid missions have been studied and are planned for the future, and MIMOS instruments among the payload such as on the Russian Phobos–Grunt will provide valuable information on their mineralogical composition.

On the basis of these applications and in particular the ongoing MER campaign, points for improvement of the instrument have been identified (e.g. Schröder *et al.* 2008c). The MIMOS instrument is continuously developed further. In MIMOS IIa, SDDs will be implemented to replace the Si-PIN diodes used as detectors in the MER design. The signal-to-noise ratio will thus be improved by an order of magnitude because SDDs offer a better energy resolution. As a result, measurement times can be shortened and/or measurements can be statistically enhanced. Another benefit of the implementation of SDDs is the possibility to simultaneously acquire XRF spectra, also for the analysis of lighter elements down to Mg. All of the example applications shown above would greatly benefit from this new instrument, MIMOS IIa. The power of combined field-portable, *in-situ*, non-destructive MB and XRF investigations has been demonstrated with MIMOS II and APXS on the Mars Exploration Rovers.



**Fig. 18.** Element ratio plots comparing two probable meteorites, Barberton and Santa Catarina to several classes of meteorites, in particular, chondrites and HEDs. Barberton was a small rock fragment and had soil in the field of view of the APXS instrument. M25 and M35 denote Barberton with 25 and 35 percent of a typical soil composition subtracted. The areas in which mesosiderites plot with increasing metal/silicate ratio are indicated where applicable (Figure adapted from Schröder *et al.* 2008b).

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## REFERENCES

- ALLEN, C.C., MORRIS, R.V. & MCKAY, D.S. 1994. Experimental reduction of lunar mare soil and volcanic Glass. *Journal of Geophysical Research*, **99**(E11), 23173–23185.
- ALLEN, C.C., MORRIS, R.V. & MCKAY, D.S. 1996. Oxygen extraction from lunar soils and volcanic glass. *Journal of Geophysical Research*, **101**(E11), 26085–26095.
- BANCROFT, G.M. 1973. *Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists*. McGraw Hill, London.
- BANIN, A. 2005. The Enigma of the Martian Soil. *Science*, **309**, 888–890.
- BANIN, A., CLARK, B.C. & WÄNKE, H. 1992. Surface Chemistry and Mineralogy. In: KIEFFER, H.H., JAKOSKY, B.M., SNYDER, C.W. & MATTHEWS, M.S. (eds) *Mars*. University of Arizona Press, Tucson, 594–625.
- BARUCCI, M.A., YOSHIKAWA, M., MICHEL, P. *ET AL.* 2009. MARCO POLO: near earth object sample return mission. *Experimental Astronomy*, **23**, 785–808.
- BLAKE, D.F., VANIMAN, D., ANDERSON, R. *ET AL.* 2009. The Chemin mineralogical instrument on the Mars Science Laboratory mission. *Lunar and Planetary Science*, **40**, 1484.
- BURNS, R.G. 1993. Mössbauer Spectral Characterization of Iron in Planetary Surface Materials. In: PIETERS, C.M. & ENGLERT, P.A.J. (eds) *Remote Geochemical Analysis: Elemental and Mineralogical Composition*. Cambridge University Press, 539–556.
- CHIARI, G. 2008. Saving art in situ. *Nature*, **453**, 159.
- CRUMPLER, L., ARVIDSON, R., BLANEY, D. *ET AL.* 2009. Field Reconnaissance Geologic Mapping of the Columbia Hills, Gusev Crater from MER Spirit Rover and HiRISE Observations. *Lunar and Planetary Science*, **40**, 2045.
- DE SOUZA, P.A. Jr, QUEIROZ, R.S., MORIMOTO, T., GUIMARAES, A.F. & GARG, V.K. 2000. Air pollution investigation in Vitória Metropolitan Region, ES, Brazil. *Journal of Radioanalytical and Nuclear Chemistry*, **246**, 85–90.
- DE SOUZA, P.A. Jr, KLINGELHÖFER, G., BERNHARDT, B., SCHRÖDER, C., GÜTLICH, P. & MORIMOTO, T. 2001. *On-line and in-situ characterization of iron phases in particulate matter*. Proceedings of the Air & Waste Management Association's 94th Annual Conference, session AB-2d, 569.
- DE SOUZA, P.A. Jr 2004. *Extraterrestrial and Terrestrial Outdoor Applications of Mössbauer Spectroscopy*. PhD thesis, Johannes Gutenberg-Universität Mainz, Germany.
- FARRAND, W.H., BELL, J.F. III, JOHNSON, J.R., ARVIDSON, R.E., CRUMPLER, L., HUROWITZ, J.A. & SCHRÖDER, C. 2008. Rock Spectral Classes Observed by the Spirit rover's Pancam on the Gusev Crater Plains and in the Columbia Hills. *Journal of Geophysical Research*, **113**, E12S38, doi: 10.1029/2008JE003237.
- FEDER, F., TROLARD, F., KLINGELHÖFER, G. & BOURRIÉ, G. 2005. In situ Mössbauer spectroscopy: Evidence for green rust (fougerite) in a gleysol and its mineralogical transformations with time and depth. *Geochimica et Cosmochimica Acta*, **69**, 4463–4483.
- FLEISCHER, I., KLINGELHÖFER, G., SCHRÖDER, C. *ET AL.* 2008. Depth selective Mössbauer spectroscopy: Analysis and simulation of 6.4 keV and 14.4 keV spectra obtained from rocks at Gusev crater, Mars, and layered laboratory samples. *Journal of Geophysical Research*, **113**, E06S21, doi: 10.1029/2007JE003022.



- FLEISCHER, I., KLINGELHÖFER, G., RULL, F. ET AL. 2010. In-situ Mössbauer spectroscopy with MIMOS II at Rio Tinto, Spain. *Journal of Physics: Conference Series*, **217**, 012062, doi: 10.1088/1742-6596/217/1/012062.
- GÜTLICH, P. & SCHRÖDER, C. 2010. Mössbauer Spectroscopy. *Bunsenmagazin*, **1/2010**, 4–22.
- HAWTHORNE, F.C. 1988. Mössbauer Spectroscopy. *Reviews in Mineralogy*, **18**, 255–340.
- HOEHLER, T.M., AMEND, J.P. & SHOCK, E.L. 2007. A “Follow the Energy” Approach for Astrobiology. *Astrobiology*, **7**, 819–823.
- KLINGELHÖFER, G., DA COSTA, G.M., PROUS, A. & BERNHARDT, B. 2002. Rock paintings from Minas Gerais, Brasil, investigated by in-situ Mössbauer spectroscopy. *Hyperfine Interactions*, **C5**, 423–426.
- KLINGELHÖFER, G., MORRIS, R.V., BERNHARDT, B. ET AL. 2003. Athena MIMOS II Mössbauer spectrometer investigation. *Journal of Geophysical Research*, **108**(E12), 8067, doi: 10.1029/2003JE002138.
- KLINGELHÖFER, G., MORRIS, R.V., BERNHARDT, B. ET AL. 2004. Jarosite and Hematite at Meridiani Planum from Opportunity's Mössbauer Spectrometer. *Science*, **306**, 1740–1745.
- KLINGELHÖFER, G., BRÜCKNER, J., D'USTON, C., GELLERT, R. & RIEDER, R. 2007a. The Rosetta Alpha Particle X-ray Spectrometer (APXS). *Space Science Reviews*, **128**, 383–396.
- KLINGELHÖFER, G., RODIONOV, D., BLUMERS, M. ET AL. 2007b. *The miniaturized Mössbauer spectrometer MIMOS II: Application for the “Phobos-Grunt” mission*. First International Conference on the Exploration of Phobos and Deimos, 5–7 November 2007, NASA Ames Research Center, Moffet Field, CA, USA, abstract #7038.
- KLINGELHÖFER, G., RODIONOV, D., BLUMERS, M. ET AL. 2008. The Advanced Miniaturised Mössbauer Spectrometer MIMOS IIa: Increased Sensitivity and New Capability for Elemental Analysis. *Lunar and Planetary Science*, **39**, 2379.
- KNOLL, A.H., CARR, M., CLARK, B. ET AL. 2005. An astrobiological perspective on Meridiani Planum. *Earth and Planetary Science Letters*, **240**, 179–189, doi: 10.1016/j.epsl.2005.09.045.
- LANDIS, G.A. 2009. Meteoritic steel as a construction resource on Mars. *Acta Astronautica*, **64**, 183–187.
- LANDIS, R.R., ABELL, P.A., KORSMEYER, D.J., JONES, T.D. & ADAMO, D.R. 2009. Piloted operations at a near-Earth object (NEO). *Acta Astronautica*, **65**, 1689–1697.
- LECHNER, P., ECKBAUER, S., HARTMANN, R. ET AL. 1996. Silicon drift detectors for high resolution room temperature X-ray spectroscopy. *Nuclear Instruments and Methods in Physics Research A*, **377**, 346–351.
- LEWIS, K.W., AHARONSON, O., GROTZINGER, J.P., SQUYRES, S.W., SCHMIDT, M.E., BELL, J.F. & CRUMPLER, L.S. 2008. Structure and stratigraphy of Home Plate from the Spirit Mars Exploration Rover. *Journal of Geophysical Research*, **113**, E12S36, doi: 10.1029/2007JE003025.
- MCCAMMON, C. 1995. Mössbauer Spectroscopy of Minerals. In: AHRENS, T.J. (ed.) *Mineral Physics and Crystallography: A Handbook of Physical Constants*. AGU Reference Shelf, vol. 2, American Geophysical Union, Washington DC, 332–347.
- MCSWEEN, H.Y., RUFF, S.W., MORRIS, R.V. ET AL. 2008. Mineralogy of volcanic rocks in Gusev crater, Mars: Reconciling Mössbauer, APXS, and Mini-TES spectra. *Journal of Geophysical Research*, **113**, E06S04, doi: 10.1029/2007JE002970.
- MING, D.W., MITTELFELDT, D.W., MORRIS, R.V. ET AL. 2006. Geochemical and mineralogical indicators for aqueous processes in the Columbia Hills of Gusev crater, Mars. *Journal of Geophysical Research*, **111**, E02S12, doi: 10.1029/2005JE002560.
- MING, D.W., GELLERT, R., MORRIS, R.V. ET AL. 2008. Geochemical Properties of Rocks and Soils in Gusev crater, Mars: Results of the Alpha Particle X-ray Spectrometer from Cumberland Ridge to Home Plate. *Journal of Geophysical Research*, **113**, E12S39, doi: 10.1029/2008JE003195.
- MITRA, S. (ed.) 1992. *Applied Mössbauer Spectroscopy: Theory and Practice for Geochemists and Archaeologists*. Pergamon Press, Oxford/New York/Seoul/Tokyo.
- MORRIS, R.V., KLINGELHÖFER, G., BERNHARDT, B. ET AL. 2004. Mineralogy at Gusev Crater from the Mössbauer Spectrometer on the Spirit Rover. *Science*, **305**, 833–836.
- MORRIS, R.V., KLINGELHÖFER, G., SCHRÖDER, C. ET AL. 2006a. Mössbauer mineralogy of rock, soil, and dust at Gusev crater, Mars: Spirit's journey through weakly altered olivine basalt on the plains and pervasively altered basalt in the Columbia Hills. *Journal of Geophysical Research*, **111**, E02S13, doi: 10.1029/2005JE002584.
- MORRIS, R.V., KLINGELHÖFER, G., SCHRÖDER, C. ET AL. 2006b. Mössbauer mineralogy of rock, soil, and dust at Meridiani Planum, Mars: Opportunity's journey across sulfate-rich outcrop, basaltic sand and dust, and hematite lag deposits. *Journal of Geophysical Research*, **111**, E12S15, doi: 10.1029/2006JE002791.
- MORRIS, R.V., KLINGELHÖFER, G., SCHRÖDER, C. ET AL. 2008. Iron mineralogy and aqueous alteration from Husband Hill through Home Plate at Gusev Crater, Mars: Results from the Mössbauer instrument on the Spirit Mars Exploration Rover. *Journal of Geophysical Research*, **113**, E12S42, doi: 10.1029/2008JE003201.
- MURAD, E. & CASHION, J. 2004. *Mössbauer Spectroscopy of Environmental Materials and Their Industrial Utilization*. Kluwer Academic Publishers, Dordrecht.
- NATHUES, A., BOEHNHARDT, H., HARRIS, A.W. ET AL. 2008. *ASTEX – An In-Situ Exploration Mission to two Near-Earth-Asteroids*. Asteroids, Comets, Meteors, 13–18 July 2008 in Baltimore, abstract #8076.
- POTTS, P.J. & WEST, M. 2008. *Portable X-ray Fluorescence Spectrometry: Capabilities for In Situ Analysis*. Royal Society of Chemistry, Cambridge.
- RIEDER, R., GELLERT, R., BRÜCKNER, J., KLINGELHÖFER, G., DREIBUS, G., YEN, A. & SQUYRES, S.W. 2003. The new Athena alpha particle X-ray spectrometer for the Mars Exploration Rovers. *Journal of Geophysical Research*, **108**(E12), 8066, doi: 10.1029/2003JE002150.
- RODIONOV, D., KLINGELHÖFER, G., BERNHARDT, B. ET AL. 2006. Automated Mössbauer spectroscopy in the field and monitoring of fougierite. *Hyperfine Interactions*, **167**, 869–873.
- RULL, F., FLEISCHER, I., MARTINEZ-FRIAS, J., SANZ, A., UPADHYAY, C. & KLINGELHÖFER, G. 2008. Raman and Mössbauer spectroscopic characterisation of sulfate minerals from the Mars analogue site at Rio Tinto and Jaroso Ravine, Spain. *Lunar and Planetary Science*, **39**, 1616.
- SCHMIDT, M.E., FARRAND, W.H., JOHNSON, J.R. ET AL. 2009. Spectral, mineralogical, and geochemical variations across Home Plate, Gusev Crater, Mars indicate high and low temperature alteration. *Earth and Planetary Science Letters*, **281**, 258–266.
- SCHRÖDER, C., KLINGELHÖFER, G. & TREMEL, W. 2004. Weathering of Fe-bearing minerals under Martian conditions, investigated by Mössbauer spectroscopy. *Planetary and Space Science*, **52**, 997–1010.
- SCHRÖDER, C., BAILEY, B., KLINGELHÖFER, G. & STAUDIGEL, H. 2006a. Fe Mössbauer spectroscopy as a tool in astrobiology. *Planetary and Space Science*, **54**, 1622–1634.
- SCHRÖDER, C., GELLERT, R., JOLLIFF, B.L. ET AL. 2006b. A stony meteorite discovered by the Mars Exploration Rover Opportunity on Meridiani Planum, Mars. *Meteoritics & Planetary Science*, **41**, Supplement, A160.
- SCHRÖDER, C., DI, K., MORRIS, R.V., KLINGELHÖFER, G., LI, R. & THE ATHENA SCIENCE TEAM 2008a. An East to West Mineralogical Trend in Mars Exploration Rover Spirit Mössbauer Spectra of Home Plate. *Lunar and Planetary Science*, **39**, 2153.
- SCHRÖDER, C., RODIONOV, D.S., MCCOY, T.J. ET AL. 2008b. Meteorites on Mars observed with the Mars Exploration Rovers. *Journal of Geophysical Research*, **113**, E06S22, doi: 10.1029/2007JE002990.
- SCHRÖDER, C., KLINGELHÖFER, G., MORRIS, R.V., RODIONOV, D.S., FLEISCHER, I. & BLUMERS, M. 2008c. Extraterrestrial Mössbauer spectroscopy: more than 3 years of Mars exploration and developments for future missions. *Hyperfine Interactions*, **182**, 149–156.
- SCHRÖDER, C., HERKENHOFF, K.E., FARRAND, W.H. ET AL. 2010. Properties and distribution of paired candidate stony meteorites at Meridiani Planum, Mars. *Journal of Geophysical Research*, **115**, E00F09, doi: 10.1029/2010JE003616.
- SQUYRES, S.W.E., ARVIDSON, R., BAUMGARTNER, E.T. ET AL. 2003. Athena Mars rover science investigation. *Journal of Geophysical Research*, **108**, 8062, doi: 10.1029/2003JE002121.
- SQUYRES, S.W., ARVIDSON, R.E., BOLLEN, D. ET AL. 2006. Overview of the Opportunity Mars Exploration Rover Mission to Meridiani Planum: Eagle Crater to Purgatory Ripple. *Journal of Geophysical Research*, **111**, E12S12, doi: 10.1029/2006JE002771.
- SQUYRES, S.W., AHARONSON, O., CLARK, B.C. ET AL. 2007. Pyroclastic Activity at Home Plate in Gusev Crater, Mars. *Science*, **316**, 738–742.
- SQUYRES, S.W., KNOLL, A.H., ARVIDSON, R.E. ET AL. 2009. Exploration of Victoria Crater by the Mars Rover Opportunity. *Science*, **324**, 1058–1061.
- WAGNER, F.E. & KYEK, A. 2004. Mössbauer Spectroscopy in Archaeology: Introduction and Experimental Considerations. *Hyperfine Interactions*, **154**, 5.
- YEN, A.S., GELLERT, R., SCHRÖDER, C. ET AL. 2005. An integrated view of the chemistry and mineralogy of martian soils. *Nature*, **436**, 49–54.