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Mössbauer spectroscopy as a tool in astrobiology

**Christian Schröder · Göstar Klingelhöfer ·
Brad E. Bailey · Hubert Staudigel**

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Abstract Two miniaturized Mössbauer spectrometers are part of the Athena instrument package of the NASA Mars Exploration Rovers, Spirit and Opportunity. The primary objectives of their science investigation are to explore two sites on the surface of Mars where water may once have been present, and to assess past environmental conditions at those sites and their suitability for life. Aqueous minerals – jarosite at Meridiani Planum, Opportunity's landing site, and goethite in the Columbia Hills in Gusev Crater, Spirit's landing site – were identified by Mössbauer spectroscopy, thus providing *in situ* proof of water being present at those sites in the past. The formation of jarosite in particular puts strong constraints on environmental conditions during the time of formation and hence on the evaluation of potential habitability. On Earth Mössbauer spectroscopy was used to investigate microbially induced changes in Fe oxidation states and mineralogy at the Loihi deep sea mount, a hydrothermal vent system, which might serve as an analogue for potential habitats in the Martian subsurface and the sub-ice ocean of Jupiter's icy moon Europa.

Key words Mössbauer spectroscopy · astrobiology · Mars · Europa · hydrothermal vent · biogeochemistry

C. Schröder (✉) · G. Klingelhöfer
Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Staudinger Weg 9, D-55128 Mainz, Germany
e-mail: schroedc@uni-mainz.de

G. Klingelhöfer
e-mail: klingel@mail.uni-mainz.de

B. E. Bailey · H. Staudigel
Institute of Geophysics and Planetary Physics, Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA 92093-0225, USA

B. Bailey
e-mail: bebailey@ucsd.edu

H. Staudigel
e-mail: hstaudigel@ucsd.edu

1 Introduction

The field of astrobiology includes the study of the origin, evolution and distribution of life in the universe. Liquid water is the fundamental ingredient without which no life-form on Earth could exist. Mars is a prime target for the search for extinct or extant extraterrestrial life because its surface exhibits abundant evidence for the presence of liquid water in the past [1]. The NASA Mars Exploration Rover (MER) twins, Spirit and Opportunity, each carry an integrated suite of scientific instruments and tools called the Athena science payload. The primary objective of the Athena science investigation is to explore two sites on the Martian surface where water may once have been present, and to assess past environmental conditions at those sites and their suitability for life [2]. Part of that instrument suite are two miniaturized Mössbauer spectrometers MIMOS II [3], one on each rover. Fe-bearing minerals identified by Mössbauer spectroscopy help to classify rocks as either igneous, sedimentary, or metamorphic. The degree of oxidation, i.e. the Fe^{3+}/Fe_{Total} ratio measured by Mössbauer spectroscopy, as well as changes in the degree of oxidation and/or in Fe-bearing mineralogy between a rock's unaltered interior and its possibly weathered surface, offer clues on past and present environmental conditions [4].

The surface of Jupiter's moon Europa is covered by a thick ice sheet, which is underlain by a globe-spanning ocean. Because this ocean environment is isolated from sunlight as an energy source, deep sea hydrothermal vent systems on Earth – such as the Loihi Seamount – might serve as an analogue for possible habitats. Fe redox reactions can be utilized by chemolithotrophic and chemolithoautotrophic bacteria as an energy source. Mössbauer spectroscopy was used to investigate Fe oxidation states in basaltic glass exposed at the Loihi Seamount [5]. In an earlier study, Agresti et al. [6], investigating material from deep-sea smoker vents by Mössbauer spectroscopy, reported superparamagnetic material correlated with anaerobic bacteria found to thrive there.

2 Results and discussion

Gusev Crater was chosen as the landing site for MER Spirit, because the inflow channel Ma'adim Vallis entering the crater from the South suggests that it may once have contained a lake. However, Mössbauer spectra of angular-shaped rocks strewn across the plains surrounding the landing sites did not show a sedimentary signature. Instead, spectra of rocks and soil were dominated by a ferrous doublet whose hyperfine parameters are characteristic of the mineral olivine (Figure 1). Olivine shows the least resistance to chemical weathering of the common rock-forming minerals. Based on the ubiquitous presence of olivine in soil, Morris et al. [7] concluded that physical (i.e., non-aqueous) rather than chemical (i.e., aqueous) weathering processes currently dominate at Gusev Crater. Des Marais et al. [8] evaluated the potential for habitable environments in the Gusev Crater plains. Aqueous alteration of minerals in ultramafic rocks, such as olivine, can produce H_2, a near-universal source of energy and reducing power for microorganisms. Such reactions would also produce magnetite. Magnetite was identified in Mössbauer spectra of rocks and soils from the Gusev Crater plains (Figure 1). However, magnetite is also produced in the formation of igneous rocks. Des Marais et al. [8]

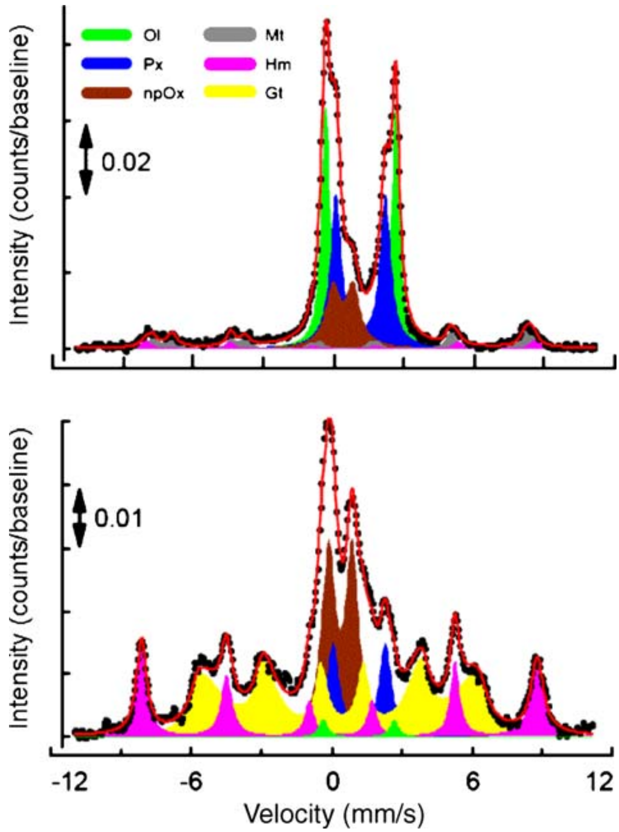

Figure 1 Typical Mössbauer spectra of basaltic soil at Gusev Crater (*top*), and of the rock Clovis in the Columbia Hills in Gusev Crater showing the highest abundance of goethite to date (*bottom*).

conclude, that although the sparsity of water puts up a barrier for life today, aquifers that were periodically recharged, for example during times of higher obliquity, might have sustained habitable conditions for geologically long periods of time. After traversing the plains surrounding its landing site, Spirit started ascending the Columbia Hills inside Gusev Crater on sol 157 of its mission. The Columbia Hills represent older terrain than the surrounding plains. Rocks encountered at the foot of the hills showed visible signs of physical and chemical weathering. In Mössbauer spectra of these rocks the mineral haematite was identified [9]. Haematite forms usually, though not exclusively, in the presence of water. In rocks showing a layered appearance further into the hills the mineral goethite was identified in Mössbauer spectra (Figure 1) [10], the first unequivocal *in situ* proof for the interaction of rocks and water in Gusev Crater. However, despite their layered appearance the goethite containing rocks do not represent sought-after lacustrine sediments [11].

Meridiani Planum was chosen as the landing site for MER Opportunity, because the area showed a clear signature of haematite in thermal emission spectra obtained from orbital observations [12]. The area surrounding the landing site is made up of basaltic soil underlain by finely layered outcrop rocks. Mössbauer spectra of the basaltic soil show the presence of olivine, and are identical to spectra obtained from soil in Gusev Crater [13, 14]. Contrary to the soil, Mössbauer spectra from the

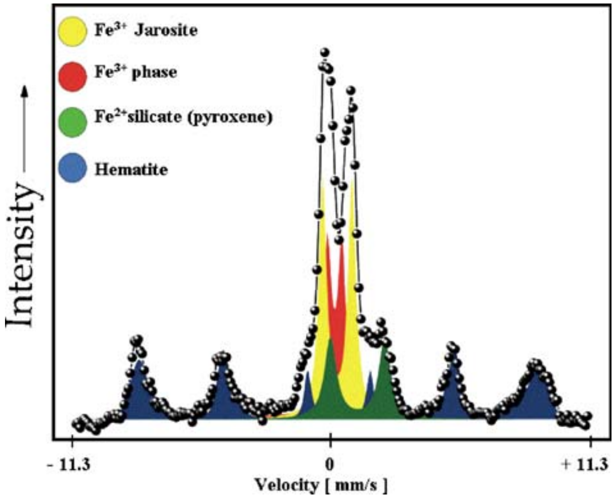

Figure 2 Typical Mössbauer spectrum of outcrop rocks at Meridiani Planum.

outcrop are dominated by a ferric doublet, whose hyperfine parameters are characteristic of the iron hydroxy sulfate mineral jarosite (Figure 2) [13]. That identification provided the first *in situ* proof, that these outcrop rocks formed in interaction with water. The uppermost layer of soil and outcrop is covered by mm-sized spherules, which appear to be weathering out of the outcrop. Mössbauer spectra of spherule-rich spots show, that they are composed mainly of haematite [13] and are thus the source of the haematite observed from orbit. The spherules likely formed diagenetically after deposition of the evaporite. Their spherical shape advocates another episode of water interaction during their formation. Based on the combined evidence from all MER instruments, Squyres et al. [15] concluded that the environmental conditions under which these sediments were laid down included episodic inundation by shallow surface water, evaporation, and desiccation, and that they were suitable for biological activity for some period of time in Martian history. Knoll et al. [16] provide an astrobiological perspective on Meridiani Planum. While Meridiani Planum may indeed have been a habitable place, high levels of acidity inferred from the presence of jarosite – jarosite forms at pH < 3.5 – would have posed a challenge for prebiotic chemical reactions thought to have played a role in the origin of life on Earth. Because sulfates and iron oxides can preserve detailed geochemical records of environmental history as well as chemical, textural and microfossil signatures of biological activity, Meridiani Planum is an attractive candidate for Mars sample return [16].

Several basaltic glass samples with varying Fe oxidation states were produced in order to detect the ability of microbial life to preferentially colonize chemically different substrates and subsequently metabolize the glass for various nutrients needed for survival. The Fe^{3+}/Fe^{2+} ratios were evaluated using Mössbauer spectroscopy [5]. Some of these basaltic glass samples were exposed to the iron-rich microbial mats and hydrothermal vent complexes at the Loihi Seamount for ~one year. Fe oxidation states were again evaluated after the exposure, showing a slight increase in Fe^{3+}/Fe^{2+} ratios. This increase may at least in part be due to strains of Fe-oxidizing bacteria that have been found on the exposed samples and have demonstrated their ability to use the basaltic glass as their only source of iron for growth [5].

3 Conclusion

Water is the most important requirement for all known life-forms. Fe-bearing minerals, goethite and jarosite in particular, identified by Mössbauer spectrometers onboard the Mars Exploration Rovers, Spirit and Opportunity, provided *in situ* proof for ancient aqueous and thus potentially habitable environments on Mars. Jarosite in particular adds acidity as a constraint to environmental conditions, which may have precluded prebiotic chemistry playing a role in the origin of life on Earth. Other minerals identified by Mössbauer spectroscopy such as olivine are a possible source of nutrients and energy.

Iron oxides can preserve signatures of biological activity, making Mössbauer spectroscopy an important tool to identify promising rocks for closer scrutiny by future dedicated biology missions to Mars, such as the planned European lander Exomars, or a Mars sample return mission.

Fe^{2+}–Fe^{3+} redox potentials are an energy source available to microorganisms at deep sea hydrothermal vent systems, which may be analogous environments compared to possible habitats in sub-ice oceans on the Jovian moon Europa. Monitoring changes in Fe^{3+}/Fe^{2+} ratios of basaltic glass samples exposed in such environments using Mössbauer spectroscopy can be used to determine the proportion of microbially induced redox reactions in such environments. The results discussed above show that Mössbauer spectroscopy is an important tool in the field of astrobiology.

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