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Mössbauer spectroscopy in astrobiology

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Introduction

Astrobiology is the study of the origin, evolution and distribution of life in the universe.[1] As such, the field begins very much on Earth before venturing out to search for life in space. This search is guided by a follow-the-water strategy because water is the most important prerequisite for the carbon-based life we know of from our own example. Two of the hot spots for this search within our Solar System are our neighbour Mars and Jupiter's icy moon Europa. Mars continues to reveal more and more morphological and mineralogical evidence for abundant water on its surface more than 3.5 billion years ago[2,3]—a time when life is thought to have begun on Earth. While the planet has become cold and arid, whiffs of methane[4–7] show that it is still active in some ways today. A biological origin of the methane has not yet been ruled out and there may be niches left on Mars that would support microbial life at the present day. Europa, on the other hand, is thought to carry a sub-surface ocean covered by many kilometres of solid ice which might be able to sustain life.

Iron is the fourth most abundant element in the Earth's crust, and iron oxides give Mars its notorious rusty-red colour (Figure 1). The materials responsible for the coloured streaks criss-crossing Europa's icy surface (Figure 2) are unknown but may also contain iron-bearing minerals. The iron sulfides mackinawite, FeS, and pyrite, FeS_2, are likely to have been around during the earliest history of Earth[8] and might have played a role in the origin of life as an energy source and by providing mineral surfaces as a template for surface metabolism.[9,10] Earth's early ocean in the absence of free oxygen was ferruginous, i.e. rich in dissolved ferrous iron (reduced iron, Fe^{2+}). Massive amounts of insoluble ferric (oxidised iron, Fe^{3+}) iron minerals deposited in Banded Iron Formations (BIFs) are thought to document the release of free oxygen from the evolution of oxygenic photosynthesis in marine cyanobacteria. However, it is debated whether the types of iron minerals found in BIFs and the ratio of ferrous to ferric iron as a redox couple reflect environmental conditions at the time of formation or whether they are a result of diagenetic processes thereafter.[11] BIFs disappear from the rock record with the great oxidation event. These days, while iron remains essential for almost all organisms as the functional centre of many proteins and enzymes, its concentrations in seawater are so low that it becomes a limiting nutrient for primary growth and therefore limits the uptake of atmospheric CO_2 by phytoplankton. There is no evidence that photosynthesis occurred on Mars and therefore, as long as there was liquid water, dissolved ferrous iron probably remained abundantly available. Similarly, Europa's ice-covered ocean would not be suitable for photosynthesis and might exhibit a ferruginous composition similar to the oceans on early Earth.

Mössbauer spectroscopy[12,13] is a powerful tool to study iron-bearing solid substances. It uses gamma-rays to probe the hyperfine interactions between the electromagnetic field of a ^{57}Fe nucleus and the electromagnetic fields of its electron shell and the next-nearest neighbours on the crystal lattice. As such it determines the oxidation states of iron, identifies iron-bearing mineral phases, and quantifies the distribution of iron between oxidation states and mineral phases. This ability does not depend on long-range ordering in a crystal lattice, which is particularly useful because many of the reactive iron species in environmental systems occur in nanoparticulate or amorphous forms. Mössbauer spectroscopy therefore has been shown to be a valuable tool in astrobiology,[14] and some of its applications in this field are demonstrated below.

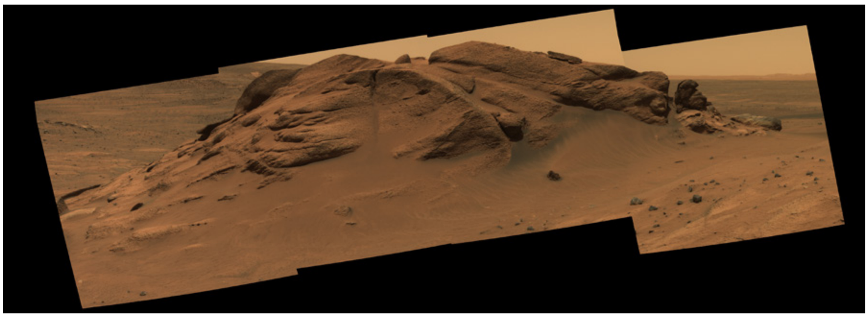

Figure 1. This mosaic of the carbonate-bearing Commanche outcrop in the Columbia Hills in Gusev Crater was acquired by the Mars Exploration Rover Spirit's Pancam on Sol 695 (16 December 2005) of its mission. The outcrop is roughly 6 m across. This approximate true colour version shows the reddish glow of iron oxide pigments in the ubiquitous dust responsible for the Red Planet's colour. Credit: NASA/JPL/Cornell/Arizona State University; http://pancam.astro.cornell.edu/pancam_instrument/images/S01695A_P2422_1_L257atc.jpg.

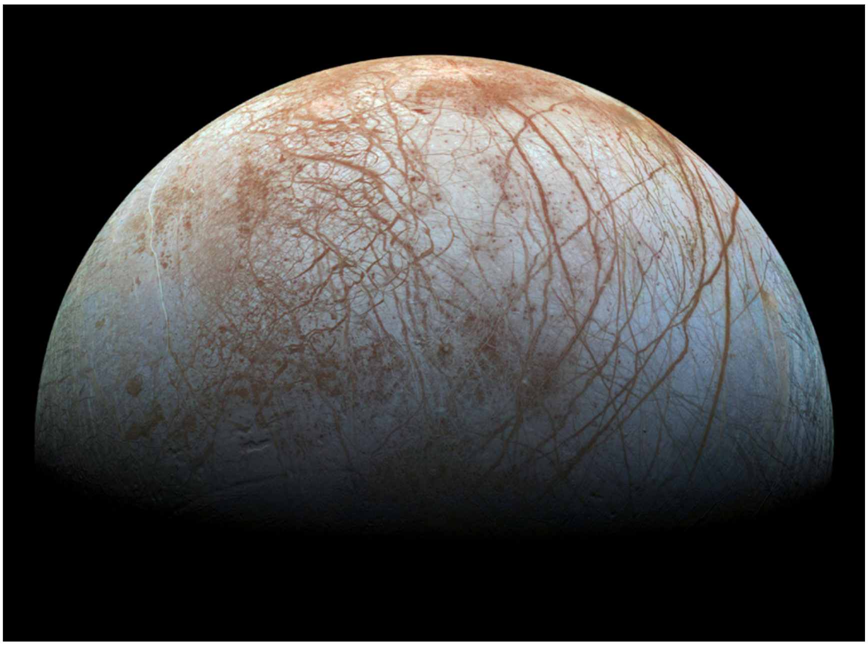

Figure 2. Jupiter's icy moon Europa is crisscrossed by long, linear cracks interrupted by regions of disrupted terrain where the surface ice crust has been broken up and re-frozen into new patterns. Colour variations across the surface are associated with differences in geologic feature type and location. For example, areas that appear blue or white contain relatively pure water ice, while reddish and brownish areas include non-ice components in higher concentrations. This true-colour view was made from images taken by NASA's Galileo spacecraft in the late 1990s. Credit: NASA / Jet Propulsion Lab-Caltech / SETI Institute; http://photojournal.jpl.nasa.gov/catalog/PIA19048.

Mössbauer spectroscopy and iron biogeochemistry on Earth

Most redox reactions in the biogeochemical iron cycle are mediated by microorganisms but compete with abiotic reactions.[15] Many microorganisms are able to use Fe^{2+} as an electron donor (iron oxidisers) or Fe^{3+} as a terminal electron acceptor (iron-reducers) instead of oxygen for respiration. Today, these processes are largely restricted to anoxic environments such as sediments or groundwater aquifers where they are energetically favourable. However, these are thought to be some of the earliest forms of respiration and likely would have been widespread on the early Earth before the rise of free oxygen.

Mössbauer spectroscopy has helped to provide new insights into how iron minerals catalyse electron transfer processes under anoxic conditions. Williams and Scherer[16] exploited the isotope selectivity—the Mössbauer effect is only observed in ^{57}Fe and Mössbauer spectroscopy is hence "blind" to ^{56}Fe—to distinguish between fractions of iron sorbed onto a mineral surface and iron within that mineral. After adding dissolved $^{57}Fe^{2+}$ to suspensions containing different ferric iron (oxyhydr)oxides synthesised with ^{56}Fe, Mössbauer spectra showed that the iron sorbed onto the mineral surface from solution becomes oxidised. Reversing the process, they showed that iron within the mineral is reduced and therefore electrons are transferred to the mineral. In a further experiment they showed that the electrons transferred were able to reduce nitroaromatic compounds, a process that they could not observe with dissolved Fe^{2+} alone, i.e. in the absence of the ferric iron (oxyhydr)oxides. A conceptual model arising from these observations[17] invokes the semiconducting properties of iron (oxyhydr)oxides. Most of the electrons transferred to the mineral do not lead to iron reduction, i.e. are localised at a single iron atom in the crystal, but are shared by the crystal in a valence band and thus free to travel to other crystal faces where they are available to participate in reductive reactions.

The mixed-valent iron oxide magnetite, Fe_3O_4, is widespread in nature and is often associated with iron metabolising microorganisms. Byrne and co-workers[18] used Mössbauer spectroscopy to quantify the distribution of iron between octahedral and tetrahedral sites in the magnetite crystal structure and, in particular, the iron oxidation states. They showed that microorganisms can use iron in magnetite both as an electron source and an electron sink. Furthermore, in co-cultures of the iron-oxidising bacterium *Rhodopseudomonas palustris* TIE-1, which is active under light, and the iron-reducing bacterium *Geobacter sulfurreducens*, which became active when the light was switched off, they showed that these processes can be cycled. Magnetite therefore acts like a natural battery.

Such electron transfer processes are not restricted to iron (oxyhydr)oxides. Iron-bearing clay minerals can also act as a renewable source of redox equivalents in anoxic environments,[19] though the process is less well understood. Neumann and co-workers,[19] for example, have used Mössbauer spectroscopy to demonstrate that a significant amount of electron transfer to structural iron in clay minerals can happen through both edge and basal planes.

Mössbauer spectroscopy on Mars

In 2003 NASA sent a pair of rovers to the Red Planet with the objective 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. Each of these Mars Exploration Rovers has a miniaturised Mössbauer spectrometer on board.[20] While the rover Spirit ceased operations in 2010, its twin Opportunity is still active exploring the Martian surface (March 2015). Their Mössbauer spectrometers have provided a wealth of astrobiologically relevant information. Here we focus on the identification of the minerals jarosite at Opportunity's landing site at Meridiani Planum and iron/magnesium-carbonate at Spirit's landing site in Gusev Crater.

Meridiani Planum is covered to a large extend by flat-lying, finely laminated sulfate-rich sedimentary rock, overlain by a thin sheet of basaltic sand. The sand sheet leaves the surface of underlying rock exposed in certain areas, and stratigraphic layers are exposed in the walls of impact craters dotted across the plains. Ripples preserved in these layers provide evidence that water not only percolated these rocks but was episodically pooling on the surface. Among the iron-bearing minerals identified with Opportunity's Mössbauer spectrometer in these rocks is the iron sulfate hydroxide mineral jarosite with the general formula $(K,Na,H_3O)(Fe_{3-x}Al_x)(SO_4)_2(OH)_6$, where $x < 1$.[2] First of all, the OH-groups in this mineral provide unequivocal mineralogical evidence that water was involved in their formation. The rock contains, on average, 2 wt% of water in jarosite alone. Second, however, jarosite forms only under acidic conditions. Low pH (and episodic water limitation also documented for this site) is not a threat to habitability as microorganisms on Earth have adapted to such conditions, but would challenge prebiotic chemical reactions that might have played a role in the origin of life on Earth.[21] High salinity/low water activity inferred from the Meridiani rock composition poses another challenge for life.[22] Taking that discussion back to iron metabolism, the presence of an active microbial iron cycle at salt concentrations close to the solubility limit of NaCl has been suggested at Lake Kasin, Russia.[23] Mössbauer spectroscopy provided evidence in the form of ferrous green rust identification against a backdrop of the ferric oxyhyxdroxide akaganéite, β-FeO(OH,Cl).

In the Columbia Hills within Gusev Crater, Spirit encountered a rock that contained ~25% carbonate (Figure 1). Carbonates also signify the presence of liquid water at the time of formation albeit this time at circumneutral pH. More significant, however, is the realisation on the basis of Mössbauer parameters (Figure 3) that this rock mainly contains low-Ca (Mg,Fe)-carbonate.[3] Its composition matches the average composition of the carbonate globules in Martian meteorite ALH84001, and carbonates identified from orbit at Nili Fossae, another location on Mars more than 6000 km distant from Gusev Crater.

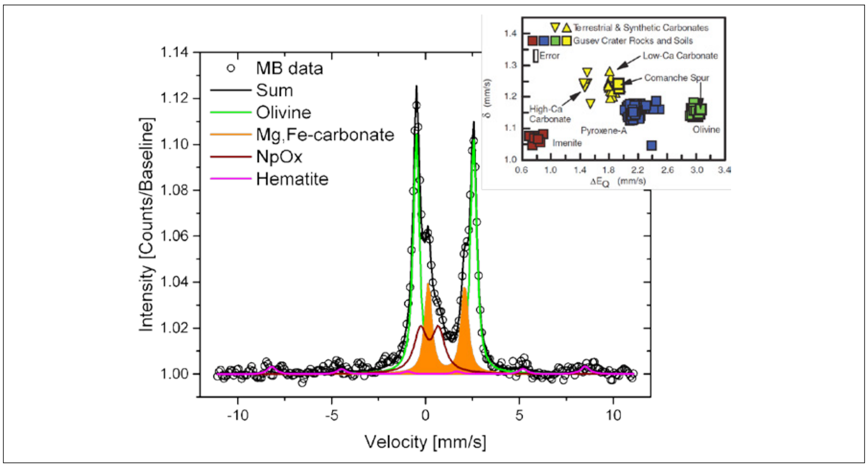

Figure 3. Mössbauer spectrum of target HorseBack on the carbonate-rich CommancheSpur outcrop in the Columbia Hills in Gusev Crater obtained by Mars Exploration Rover Spirit. The Mg,Fe-carbonate is highlighted as filled orange sub-spectrum. The inset shows the Mössbauer parameter space of isomer or chemical shift δ versus quadrupole splitting ΔE_Q. Particular minerals measured in different samples cluster in this diagram, which clearly shows that high and low-Ca carbonates occupy distinct areas.

This argues for processes operating on a global scale ~4 Ga ago on the basis of the age of ALH84001. This time was during the Noachian period, the earliest and wettest of Mars' three geologic eras. The Noachian is often characterised by abundant deposition of clay minerals. Evidence from orbiters and NASA's latest Mars rover Curiosity suggests that these clay minerals too contain magnesium and iron as dominant cations. On Earth, on the other hand, carbonates occur generally as high-Ca variants calcite or aragonite, both $CaCO_3$ but with different crystal structures, or dolomite, $(Ca,Mg)CO_3$, which reflects the low solubility of iron in an oxygenated environment.

Mössbauer spectroscopy on Europa?

Little is known about the composition of the inferred sub-surface ocean on Jupiter's icy moon Europa. Iron should be abundant in its rocky mantle and might be dissolved in the overlying ocean because free oxygen is unlikely. Oxygenic photosynthesis is not feasible under the thick ice sheet. Tidal forces from Jupiter's gravitational pull may keep volcanism active and it is intriguing to hypothesise the presence of hydrothermal vents on Europa's ocean floor. Deep sea hydrothermal vents on Earth support whole ecosystems and might also be the place where life on Earth originated.[24] Both iron oxidisers[25] and iron reducers[26] are active at such vents.

Both NASA and the European Space Agency are currently developing concepts to study Jupiter's icy moons in general and Europa in particular. A lander investigating the minerals and iron oxidation states deposited along cracks in the icy surface *in situ* would provide a wealth of information on the sub-surface ocean and hence the assessment of the potential habitability of Europa. Could such a lander carry a Mössbauer spectrometer?

Europa may be on the very edge of the places possible to be explored *in situ* with this technique.[27] This is largely dictated by the half-life of the ^{57}Co source. The decay of this isotope provides the characteristic gamma-radiation needed for ^{57}Fe Mössbauer spectroscopy. Its half-life of 270 days is on the order of the length of a journey to Mars. NASA's Galileo spacecraft took almost six years, however, to arrive at the Jupiter system. Nevertheless, the Mars Exploration Rover Mössbauer spectrometers were working for approximately that timescale, though spectral acquisition had become a lengthy process due to the low activity of the source at that point. New technical developments may extend the lifetime yet a little further. Replacing the Mars Exploration Rover Mössbauer spectrometers' silicon PIN diode detectors with silicon drift detectors reduces the background noise in spectra because of the latters' improved energy resolution. This allows for faster acquisition of statistically meaningful Mössbauer spectra and, as an added bonus, X-ray fluorescence spectra to analyse elemental composition can be obtained with the same instrument.[28,29]

Summary

The redox-active element iron and iron-bearing minerals are thought to have played an essential role in the origin and evolution of life on Earth. Even after the great oxidation event and the removal of almost all dissolved iron from the world's oceans, the biogeochemical iron cycle continues to exert a controlling influence on other elemental cycles such as the global carbon cycle. Mars and Europa are the two bodies in our solar system with the highest astrobiological potential. Iron-bearing minerals have dominated on Mars throughout its history, not least by giving the Red Planet its characteristic colour. It is not unreasonable to think that iron also plays a prominent role in Europa's sub-surface ocean.

Mössbauer spectroscopy is a powerful tool to investigate iron-bearing solids. The technique enables the determination of iron oxidation states, the identification of iron-bearing mineral phases, and the quantification of the distribution of iron between oxidation states and mineral phases.

Applying Mössbauer spectroscopy in contemporary settings to further elucidate the driving forces behind the biogeochemical iron cycle is essential to understand the processes underlying the origin and evolution of life on the early Earth. From there, the suitability for life of other bodies in our Solar System such as Mars or Europa can be assessed.

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