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Validating the performance of a Raman laser spectrometer (RLS) instrument under Martian conditions

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Chapter 1: Introduction to Mars

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1.1 Introduction to the planet Mars

Mars is the closest planet to Earth. It is known as the “Red Planet” due the presence of iron oxide on the surface. It is the fourth planet in our solar system relative to the Sun. Mars also has two small moons that are named Phobos and Deimos. They orbit the planet at a relatively close distance of 9377 and 23436 km respectively.

Mars is a rocky differentiated planet like Earth divided into a crust, a mantle and a core. Figure 1.1 shows the internal structures of Mars and Earth.

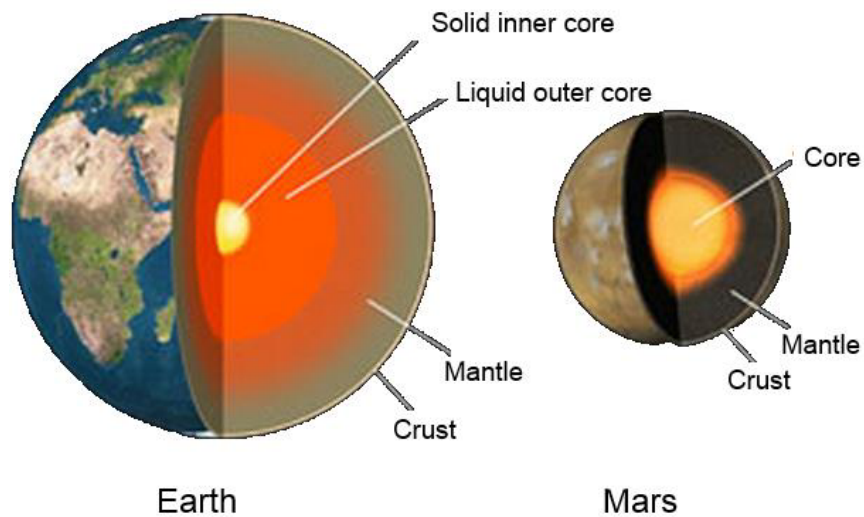


Figure 1.1. The internal structure of Mars and Earth (modified from <http://www.rationalskepticism.org>).

Mars diameter (3390 km) is approximately half that of Earth's. Due to its lower mass its surface gravity is about three times less than on Earth.

Mars rotates about its own axis in 24 hours, 39 minutes and 35 seconds, which is a solar day. Because Mars is more distant from the sun, it takes longer to orbit around the sun. Mars completes an orbit in 669 Martian days. Table 1.1 contains a summary of the comparison of physical parameters of the planets Mars and Earth.

Parameters	Mars	Earth	Ratio (Mars/Earth)
Mass (10^{24} kg)	0.64185	5.9736	0.107
Volume (10^{10} km ³)	16.318	108.321	0.151
Equatorial radius (km)	3396.2	6378.1	0.532
Core radius (km)	1700	3485	0.488
Mean density (kg/m ³)	3933	5515	0.713
Surface gravity (m/s ²)	3.71	9.80	0.379
Black-body temperature (K)	210.1	254.3	0.826
Incident flux (W/m ²)	600	1400	0.428
Surface temperature (°C)	-63 (-133 to +27)	15 (-89 to +60)	-
Surface pressure (mbar)	6 to 10	1013	-
Moon(s)	Phobos and Deimos	The Moon	-
Distance to the Sun (10 ⁶ km)	228 (1.5AU)	150 (1AU)	-

Table 1.1. Comparison of the major physical parameters of Mars and Earth.

1.2 Present climatic conditions at the Mars surface

In this section Martian environmental conditions are reviewed. This introduction is essential as we need to simulated these conditions in MASC to determine the RLS instrument performance under Martian conditions.

1.2.1 Mars' atmosphere

The Mars atmosphere is approximately 100 times thinner than on Earth. It consists of approximately 95% carbon dioxide. Table 1.2 shows the exact Martian atmospheric compositions.

	Mars	Earth
CO ₂	95.32	0.039
N ₂	2.7	78.084
Ar	1.6	0.934
O ₂	0.13	20.946
CO	0.08	4.0673
H ₂ O	0.021	0.40 in entire atmosphere, typically 1– 4 at surface
Ne	0.00025	0.001818
Kr	0.00003	0.000114
Xe	0.000008	0.000009
O ₃	0.000003	0.0000006

Table 1.2. Comparison of the atmospheric compositions of Mars and Earth (in percent) (Kieffer et al., 1992).

1.2.2 Temperature and climate at the Mars surface

Due to the thin atmosphere, Mars is not able to retain much of the heat from sunlight. Most of the heat comes from the ground after it absorbs solar radiation. The Martian atmosphere does not have enough absorption or greenhouse capability to contribute to the warming of the surface. On Earth the presence of water and carbon dioxide in its atmosphere are the most common contributors of the greenhouse effect, Fig. 1.2. When sunlight comes through the atmosphere, some solar radiation is reflected from the Earth's surface and as a result sunlight energy is sent back to the atmosphere. However, sunlight radiation is partially absorbed at the Earth's surface and in the atmosphere. This radiation warms up the planet and is later re-emitted as infrared (thermal) radiation. The presence of water and carbon dioxide in Earth's atmosphere leads to the absorption of some of this infrared radiation. These characteristics are the main contributors to the planets greenhouse effect, which is demonstrated in Fig. 1.2.

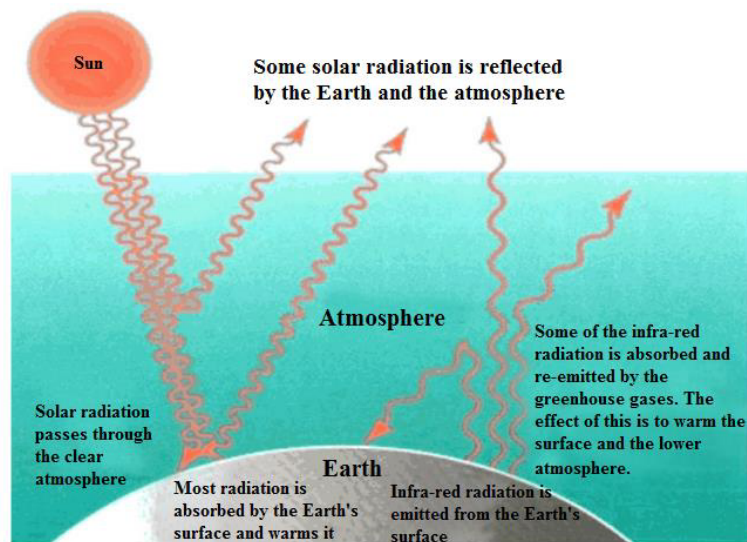


Figure 1.2. The greenhouse gases trap some of the reflected solar heat in the atmosphere and raise the average temperature of the Earth's surface from about $-21\text{ }^{\circ}\text{C}$ to about $+14\text{ }^{\circ}\text{C}$ (modified from <http://www.is.wayne.edu/MNISSANI/A&S/greenhou.htm>).

The average temperature on Mars is about $-60\text{ }^{\circ}\text{C}$. As Mars orbits around the sun with a tilt angle of 25.19° on its rotational axis, Mars has seasons like Earth (Earth has a tilt angle of 23.44°). Because Mars is further away from the sun, seasons are longer. In the Northern Hemisphere, spring lasts seven months, while summer and fall are both about six months long, and winter only four months long (Earth months). According to the Mars Orbiter camera, in the summer the temperature can reach $\sim 30\text{ }^{\circ}\text{C}$ at the equator, while in the winter the temperature drops to $\sim -130\text{ }^{\circ}\text{C}$ at the poles (Grady, 2008).

Rovers and landers have provided precise temperature records at local sites on Mars, for instance the Curiosity rover has been performing daily measurements since 2012. These data show there is a diurnal temperature variation of more than $80\text{ }^{\circ}\text{C}$. The thin Martian atmosphere cannot retain the heat during the night. Figure 1.3 reports the data collected by the Curiosity rover between August 2012 and February 2013 at the Gale Crater.

However, the diurnal temperature change can be narrowed to only about $10\text{ }^{\circ}\text{C}$ during periods of dust storm (Sheehan, 1996).

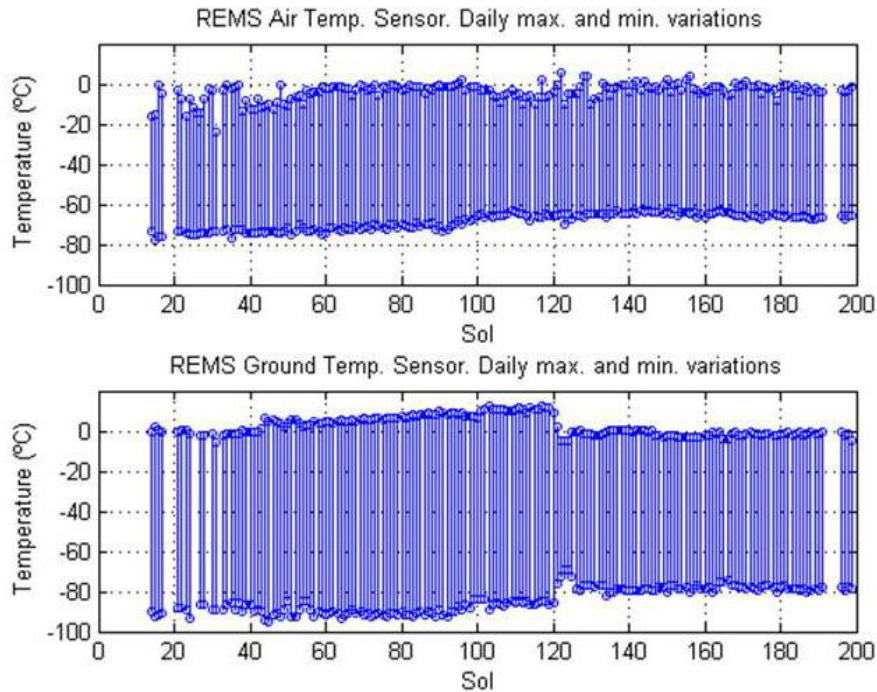


Fig. 1.3. Temperature measured by Curiosity rover from mid-August 2012 to late February 2013 at the Gale Crater. The upper graph shows the daily minimum and maximum of air temperature around the rover. The lower graph shows daily minimum and maximum of ground temperature measured by Rover Environmental Monitoring Station (REMS). Image credit: NASA, <http://photojournal.jpl.nasa.gov/catalog/PIA16913>.

Curiosity measured temperatures above 0 °C on Mars. This is one of the conditions where liquid water could be present. Nevertheless, liquid water is not stable in the planet because the atmospheric pressure is below the water triple point: any liquid water would immediately sublime into vapour.

1.3 Age of Mars' surface

A common way to estimate the age of planetary surfaces is counting the number of craters. These craters have formed due to meteorite bombardments. When applied to Mars, this method resulted in the separation of the geologic history of the planet into three major periods: the Noachian, Hesperian and Amazonian (Tanaka, 1986; Scott and Tanaka, 1986; Tanaka et al., 1992). The Noachian is the oldest period of Mars history. It began at the origin of Mars and extended to ~ 3.9 Ga. The Noachian period was followed by the Hesperian, from ~ 3.9 to 3.0 Ga. The last period is the Amazonian, from ~ 3.0 Ga to the present. Figure 1.4 shows the map of the ages of the Martian surface.

Noachian: The name Noachian was chosen because of the high density of craters in the terrains of the Noachis Terra. This period is characterized by the highest density of meteorite impacts.

Hesperian: The Hesperian era is named after Hesperia Planum, a cratered highland region northeast of the Hellas Basin. This era is characterized by a lower density of craters but marked volcanic activity. It represents most of the lava plains in the northern hemisphere.

Amazonian: The most recent era, the Amazon, is named after Amazonis Planitia, which has a sparse crater density over a wide area. Such densities are representative of many Amazonian-aged surfaces. The Amazonian era is characterized by the lowest density of craters and corresponds mainly to the formation of the huge volcano Olympus Mons, the formation of landslides in the Valles Marineris, and the formation of the broad plains and sand dunes near the Martian poles.

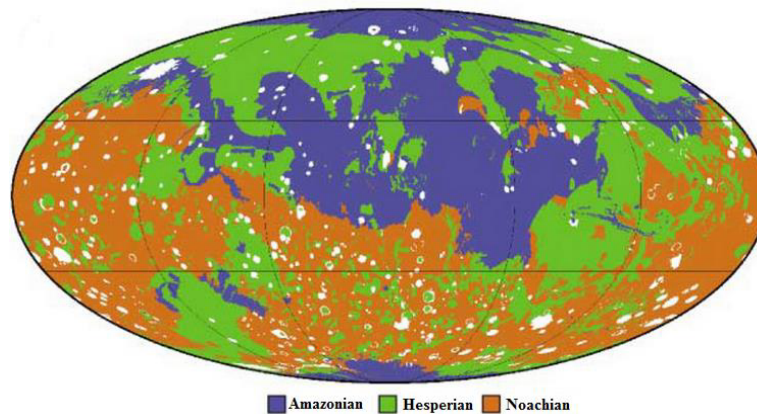


Figure 1.4. Map of the ages of the Martian surface, areas in white are impact craters and their ejecta deposits (Greeley and Guest, 1987; Scott and Tanaka, 1986).

Lunar studies have contributed to quantitative age estimations. The crater density on the Moon has been calibrated with absolute ages determined on samples returned by Apollo and Luna missions. For that study, the crater densities were measured at landing sites and radiometric ages were determined on returned samples. Therefore, the direct relationship between crater densities and absolute ages can be estimated. The lunar crater chronology provides rough measurements of absolute ages for the entire surface of the moon (Hartmann, 1970; Neukum and Ivanov, 1994; Neukum et al., 2001; Stöffler and Ryder, 2001). The lunar absolute chronology method has been transferred to Mars, taking into account the closeness of Mars to the main asteroid belt, the Martian gravity and the effect of the Martian atmosphere (Hartmann, 1999, 2005; Neukum et al., 2001; Ivanov, 2001; Hartmann and Neukum, 2001). In this manner absolute ages can also be estimated for Mars surfaces. Considering the margin of error in the age estimation, the boundary between the Noachian, the earliest period, and the Hesperian, is estimated to be between 3.5 Ga and 3.7 Ga. The

boundary between Hesperian and Amazonian is between 3 Ga and 2.9 Ga (Hartmann and Neukum, 2001; Ivanov, 2001; Werner, 2005).

1.4 Mars' composition and surface mineralogy

Although there are no samples directly returned from the Martian surface, there are Martian meteorites that provide data on the chemical composition of Mars. The composition of Mars was also inferred from the data collected from a number of successful missions. These data were collected from several instruments such as spectrometers on board of spacecrafts, remote sensing from orbit or *in situ* analyses on the Martian surface. The data confirmed the detection of not only magmatic minerals and rocks but also hydrated minerals, sedimentary and evaporite deposits (sulphates, carbonates). One of the objectives of this research is to determine if the RLS instrument is capable of identifying minerals which have been detected on Mars and if it is possible to determine compositional variations within individual mineral groups. Hence the major minerals that are found on Mars are summarized in this section. The accurate identification of these minerals by the RLS instrument can help to better understanding the geology history of Mars, its evolution and give clues about the present or past signs of life on Mars.

1.4.1 Magmatic rocks

1.4.1.1 Information from Martian meteorites

Martian meteorites were ejected from Mars by the impact of a comet or an asteroid and subsequently landed on Earth. There are currently around 120 meteorites that have been identified as Martian meteorites. The fact that they derive from Mars is based on elemental and isotopic compositions that are similar to rocks on Mars. They contained trapped gases (as bubbles) from which the composition is similar to the Martian atmosphere as measured by the Viking lander (Bogard and Garrison, 1999). Martian meteorites are classified into three main categories: Shergottites, Nakhilites and Chassignites (SNC). They are mafic and ultramafic igneous rocks and have compositions close to terrestrial basalts, clinopyroxenites and dunites. The infamous meteorite called ALH84001 is also assumed to be from Mars but cannot be classified into one of these categories as it has a distinct composition and age. The classification of Martian meteorites is as follows:

a) Shergottites

Shergottites are named after the Shergotty meteorite, which fell at Sherghati, India in 1865. Shergottite consists mostly of olivine, pigeonite (a pyroxene mineral) and plagioclase feldspar, making it a basalt. Basaltic shergottites have volcanic effusive textures. They contain clinopyroxene and plagioclase. According to most authors these meteorites are considered young (younger than other meteorites, < 500 Ma), while the Martian surface is generally very old (about 90% of the surface is > 3 Ga) and has only a few terrains that

belong to the Amazonian era (Hartmann and Neukum, 2001). The age of Shergottites is still a subject for discussion.

b) Nakhrites

The Nakhla meteorites are named after a fall that occurred in El Nakhla, Egypt, in 1911. They are clinopyroxenites with a fine-grained texture. They consist primarily of green cumulate augite crystals with minor olivine in a very fine-grained mesostasis. These rocks were formed by slow cooling, possibly in the subsurface. They are estimated to have formed around 1.3 Ga (Bouvier et al., 2005).

c) Chassignites

This group is named for its only member, Chassigny, a meteorite that fell in France in 1815. Chassigny is a cumulate rock, resembling a terrestrial dunite. It consists of 91% iron-rich olivine, 5% clinopyroxene, 1.7% plagioclase, 1.4% chromite, 0.3% melt inclusions and other accessory minerals and phases (Nyquist et al., 2001; Bouvier et al., 2005). Its age is about 1.36 Ga and its compositional and elemental trends, indicate that Chassignites and Nakhrites may have been formed by similar magmatic processes.

d) ALH84001

The Antarctic meteorite Allan Hills 84001 was found in late 1984. Orthopyroxenite ALH84001 has a crystalline structure and was estimated to have formed 4.09 Ga (Bouvier et al., 2009; Lapen et al., 2010). It contains carbonates that were initially reported to be Martian fossils (McKay et al., 1996) but further studies have brought this interpretation into question (Fig. 1.5) (Golden et al., 2001; Treiman and Essene, 2011).

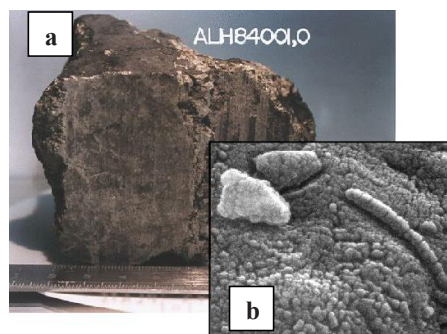


Figure 1.5. Images of a) the meteorite ALH84001 and b) electron microscope view. Nanoscale tubular structures were first interpreted as potential bacteria (McKay et al., 1996).

1.4.1.2 Information from space missions

Telescopic observations of the Martian surface have revealed the bright reddish areas covered by oxidized iron dust (hematite). The darker areas also contain minerals that are more difficult to oxidize (like pyroxene or olivine). These minerals are typical constituents of basalts on Earth.

Analyses from spacecrafts have provided additional information. Phobos 2 identified unoxidized volcanic pyroxenes in Mars dark regions, while hematite and even goethite were identified in brighter regions. Subsequently, thermal emission spectrometer (TES) aboard Mars Global Surveyor, confirmed the presence of pyroxene bearing rocks, which depending on the region, could be basalts or andesite. This instrument also detected some olivine rich regions.

The Sojourner micro-rover aboard the Pathfinder lander analysed volcanic rocks on the Martian surface. In addition to oxidized iron minerals and contrary to what one would expect from Martian meteorites, the detected volcanic rocks have a higher silicon content than basalt and are therefore classified as andesite. However, the instruments aboard the rover could only assess the global compositions of rocks and could not precisely identify minerals. These analyses were limited to the region of Chryse Planitia (26.7° N et 320° E) and does not exclude the presence of basalts in others Martian regions.

The Spirit and Opportunity rovers carried instruments that were able to identify minerals and analyse rock composition. The Spirit rover discovered unoxidized olivine and pyroxene bearing basaltic rocks in the Gusev Crater. It also identified ilmenite (FeTiO_2) in some areas. These oxidized minerals were also a major component of the dust covering those rocks. Similarly, the Opportunity rover landed in the dark region called Sinus Meridiani and discovered basaltic, olivine-rich dust, sand and cobbles. In this study, we will try to identify basaltic magmas such as olivine with the RLS instrument. Results are reported in chapter four of this thesis.

The presence of unaltered volcanic rocks on the Martian surface indicates that the Mars environment was quite dry and cold throughout the recent history of the planet. However, in addition to these magmatic rocks and minerals, coarse grained hematite, sulphates, hydrated minerals, sedimentary and evaporitic rocks have been identified. Their presence suggests that past aqueous activities occurred on the planet.

1.4.2 Minerals and rocks suggesting past aqueous activities at Mars' surface

The past aqueous activity can be detected from the composition of minerals such as carbonates, phyllosilicates and hydrated sulphates, which have been detected on Mars.

Carbonate is a weathering product of water and basalt in an atmosphere with CO_2 (Gooding, 1978; Catling, 1999). Carbonates are detected locally on the surface of Mars and within Martian meteorites (Bridges et al., 2001) and at less than 5% abundance in Martian dusts

(Pollack et al., 1990; Bandfield et al., 2003). During the Noachian era, water was assumed to have a neutral to alkaline pH. This suggestion is based on the presence of carbonates and clays. It also indicated that acidic weathering that is characteristic for the later Hesperian era did not dominate all aqueous environments, as it did not destroy all of these carbonates (Fairén et al., 2004).

The OMEGA visible and infrared mapping spectrometer has mapped almost the entire surface of Mars during the last 10 years. OMEGA has detected phyllosilicates and hydrated sulphates over large, but isolated, areas on the surface (Fig. 1.6). Phyllosilicates such as clay are alteration products of igneous minerals as a result of long-term contact with water (at alkaline pH). In contrast, hydrated sulphates are formed through rock interaction with acidic water. Phyllosilicates and sulphates are both a sign of the existence of water in active geochemical reactions. Compared to the presence of ferric oxide on the Martian surface today, the presence of phyllosilicates and sulphates in older landscapes suggests a transition from a wet to a dry climate over time (Bibring et al., 2006). The sulphates found on Mars come from the Hesperian era. Sulphates are not found in the Noachian era. This suggests that processes such as evaporation, crystallization and weathering were only present in the Hesperian era, probably as a result of volcanic activity and heating of the planet in general.

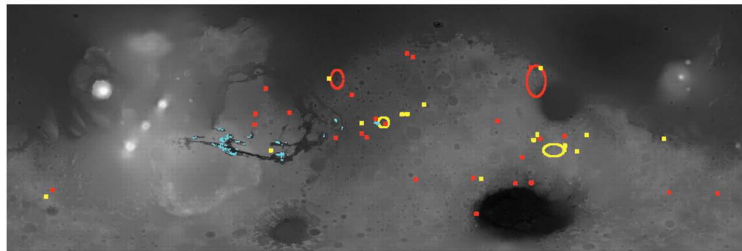


Figure 1.6. Detection of hydrated minerals by OMEGA, reported on a MOLA (Mars Orbiter Laser Altimeter) elevation map (black = low, white = high). Phyllosilicates are shown in red and sulphate is shown in blue. Other undetermined hydrated minerals are indicated in yellow (Bibring et al., 2006).

In addition the TES spectrometer of Mars Global Surveyor detected coarse-grained hematite. On Earth this kind of hematite is formed under the action of liquid water. The most hematite rich region is close to 0° longitude on Mars. This site was selected for landing the Opportunity rover. Confirming TES findings, Opportunity rover identified 2-5 mm sized hematite grains, probably eroded from layered sedimentary evaporates, containing also the hydrated ferric sulphate jarosite. Aqueous activities have the possibility to have created an environment favourable for life on Mars. Therefore, in this study we tried to identify a group of hydrated minerals with the RLS instrument. Results are reported in chapter five of this thesis.

Currently the Mars Science Laboratory robot (Curiosity) is also collecting data from Mars planet. The data will be reviewed further in this chapter.

1.5 The Mars climate and its evolution

Figure 1.7 presents a summary of characteristic features associated with the three main Martian eras. During the Noachian era the following occurrences took place:

- Formation of valleys
- Formation of craters
- Formation of phyllosilicates
- Formation of oceans and lakes
- Heavy volcanic activity (in the late Noachian)

The end of the Noachian era, which coincides with the start of the formation of the Tharsis volcanic dome, marked a global climate change in which water gradually disappeared from the surface. The weathering and erosion by water is evidence of the presence of water in the Noachian era (Carr and Head, 2010). Valleys in the Noachian era gradually disappeared. Outflows channels with intense flows of water started to emerge in the Hesperian era (Baker, 1982). These channels existed for only brief periods in this era. The mineralogy recorded in sedimentary deposits that belong to the Hesperian era changed from containing phyllosilicates to sulphates.

For the Hesperian era the following occurrences took place:

- Decline of all the activities that are mentioned in the Noachian era
- Climate changed to become more dry and dusty
- Formation of lava plains
- Formation of sulphates (instead of phyllosilicates)

Liquid water and hydrated deposits disappeared quickly from the surface of Mars after the Hesperian era. This suggests that the planet was dry over the last ~ 3.0 Ga (throughout the Amazonian period).

For the Amazonian era, which is the latest era, the following occurrences took place:

- Climate changed to be more cold
- Formation of a lithosphere
- Formation of landslides in Valles Marineris
- Formation of broad plains
- Formation of sand dunes near Martian poles.

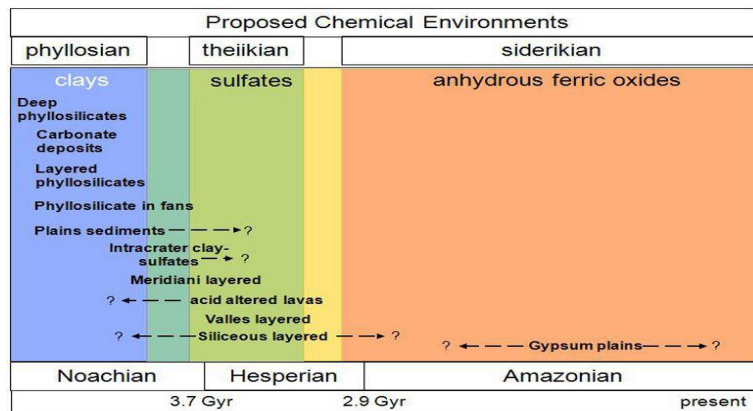


Figure 1.7. Diagram showing the evolution of the morphologies and weathering conditions that were observed at the surface of Mars over time. It also includes a mineralogical timeline that divides Mars into a phyllosian, theiikian and a siderikian period. These names are based on the minerals that are mostly found in each of these periods (Murchie et al., 2009).

The presumed existence of greenhouse conditions in the early Martian history made the Martian climate more hospitable in the past. The inferred denser atmosphere appears to have disappeared in the late Noachian era either through chemical reactions with the surface and/or gravitational escapes.

1.6 Search for life beyond Earth on Mars: Mars missions

Mars has been the subject of several missions since space exploration began. They can be briefly summarized as follows:

Currently active missions: Curiosity, Mars Reconnaissance Orbiter, Mars Exploration Rover Opportunity, Mars Exploration Rover Spirit, Mars Express, 2001 Mars Odyssey

Future missions: ExoMars, Maven, Mangalyaan

Past missions: Phobos, Grunt, Yinghuo-1, Phoenix, Mars Exploration Rover Spirit, Mars Polar Lander, Nozomi, Mars Climate Orbiter, Mars Pathfinder and Sojourner, Mars 96, Mars Global Surveyor, Mars Observer, Phobos 2, Phobos 1, Viking program, Mars 4, 5, 6 and 7, Mars 2 and 3, Mariner 9, Kosmos 419, Mariner 8, Mars 1969a and b, Mariner 6 and 7, Zond 2, Mariner 4, Mariner 3, Mars 1, Korabl 11 and 13, Korabl 4 and 5.

In total 50 missions were sent to Mars and only 21 of those missions made it to the planet. Table 1.3 shows an overview of the (relatively) successful missions that made it to Mars, their scientific goals and the result of these missions:

Launch Date	Name	Country	Type	Scientific goals	Result of the mission
1964	Mariner 4	US	Flyby	Making observations of Mars and transmit them back to Earth	First images of the Martian surface were taken
1969	Mariner 6 & 7 (dual mission)	US	Flyby	Analysing the atmosphere and the surface. (Equipped with an ultraviolet spectrometer)	Photographed about 20 percent of the planet's surface
1971	Mars 3 Orbiter/Lander	USSR	Landing	- Analyse the soil composition - Monitor solar radiation & wind - Monitor interplanetary and Martian magnetic fields	Transmission stopped after 14.5 seconds during its descent (5.7 km/s)
1971	Mariner 9	US	Orbit	Map over 70% of the Martian surface	- First spacecraft to orbit Mars - The 7329 images, covering about 80% of the planet - A lack of evidence for volcanic activity - Atmospheric pressures ranging from 2.8 to 10.3 mbar, measurements of atmospheric water vapour content - An ultraviolet spectrum of Phobos
1973	Mars 5	USSR	Orbit	- Orbiting the planet - Serving as a communication station for other Russian Martian explorers	Mission considered a failure. Only 22 loops around the planet were done
1973	Mars 6 Orbiter/Lander	USSR	Landing	- Performing a soft landing - To study proton and electron fluxes from the Sun	Lander smashed to the surface 5 minutes after entering Mars' atmosphere
1975	Viking 1 Orbiter/Lander	US	Landing	Researching the possibility of life on Mars	-First successful soft landing on the surface of Mars Measurements were made of : - The atmospheric composition - The surface elemental abundance - Temperature of the surface and meteorological conditions
1975	Viking 2 Orbiter/Lander	US	Landing	Further exploration of Mars as part of the Viking program	Discovery of river valleys
1996	Mars Global Surveyor	US	Orbit	Making observations of Mars at a height of 400 km	Discovery of landforms that were a result of weathering and winds
1996	Mars Pathfinder	US	Landing	- Making measurements of the atmosphere during its descent and sending these back to Earth - Conducting experiments to the soil with new equipment	Data showed that the central metallic core is between 1300 km and 2000 km in radius

2001	Mars Odyssey	US	Orbit	<ul style="list-style-type: none"> - Creating a map with chemical compounds of the surface of Mars - Trying to find water ice - Determining the radiation intensity in deeper layers 	Retrieved data indicated the presence of water on Mars
2003	Mars Express Orbiter/Beagle 2 Lander	ESA	Landing	Studying interior, subsurface, surface and atmosphere, and environment of the planet Mars	<ul style="list-style-type: none"> - Discovery of water on the South Polar ice cap, consisting of carbon dioxide (85%) ice and water ice (15%) - Detection of methane and ammonia in the atmosphere
2003	Mars Exploration Rover – Spirit (MER A) Opportunity (MER B)	US	Lander	Further exploration of the geology of Mars, mainly looking for traces of water and characterising rocks and soils	<ul style="list-style-type: none"> - Found traces of water in the rocks of the Gusev Crater - Landing site turned out to be a place where a sea or a lake existed (Meridiani Planum)
2005	Mars Reconnaissance Orbiter	US	Orbit	<ul style="list-style-type: none"> - Identifying possible future landing sites - Identifying locations where liquid water existed (possible life forms) - Gain more knowledge of the climate on Mars 	Found large amounts of lava traces (Cerberus Palus)
2007	Phoenix Mars Lander	US	Lander	Studying the Polar cap area of Vastitas Borealis to see if life existed in the past	Confirmation of the presence of water by Nasa
2011	Mars Science Laboratory	US	Lander	<ul style="list-style-type: none"> - Preparing a manned mission to mars - Studying the climate and geology - Determining if life could have been possible in the past 	<ul style="list-style-type: none"> - Evidence for atmospheric loss - Evidence for ancient water - Evidence for ancient habitability

Table 1.3. The (relatively) successful missions and their scientific goals and results.

1.6.1 Mars Science Laboratory, Curiosity rover

Mars Science Laboratory (MSL) mission was launched in November 2011 and reached its destination in August 2012. The MSL rover, Curiosity, is about 6 times bigger than the Mars Exploration Rovers (MER) (Fig. 1.8). The MSL landed at the Gale Crater. The crater was chosen for study because of the presence of both clays and sulphate minerals, which are formed under different conditions in the presence of water. Water is a key ingredient of life as we know it and the history of water in the Gale Crater, based on rock material, will give Curiosity clues to a possible habitat for life.



Figure 1.8. Comparison of the Mars Exploration Rovers (MER) robot (Spirit and Opportunity left) with the robot Pathfinder (Sojourner, centre) and the Mars Science Laboratory robot (Curiosity, right) (Credit: Jet Propulsion Laboratory (JPL))

The Mars Science Laboratory rover was built to investigate the recent and ancient habitable environments (Grotzinger et al., 2012). Curiosity is designed to assess whether the Martian environment ever was/is capable of supporting microbial life. The goal of the instruments onboard Curiosity is to characterize the geology, the atmosphere, the environmental conditions and to identify potential bio signatures. Curiosity will have a lifetime of at least one Mars year (~ 23 months), and has the capability to cross a distance of at least 20 km. The MSL science payload was reviewed in the work of Grotzinger et al., 2012 and includes:

- A laser induced breakdown spectrometer (LIBS) to analyse the chemical composition of minerals and rocks (ChemCam) (Meslin et al., 2013),
- An active neutron spectrometer to search for water in rocks/regolith (DAN)
- A weather station to assess modern-day environmental variables (REMS)
- A gas chromatograph-mass spectrometer and gas analyser that will search for organic carbon in rocks, regolith fines and the atmosphere (SAM) (Mahaffy, et al., 2012)
- An X-ray diffractometer that will verify mineralogical diversity (CheMin)(Bish et al., 2013)
- Focusable cameras that can image in natural colour (Mastcam, MAHLI)(Edgett, 2012)
- An alpha-particle X-ray spectrometer for *in situ* identification of rock and soil chemistry (APXS)
- A sensor designed for continuous detecting of background solar and cosmic radiation (RAD)

As the RLS instrument and the ChemCam instrument use a LIBS spectrometer, the ChemCam instrument will be briefly explained in this chapter but the principles of the LIBS technique are presented in more detail in chapter two. The ChemCam (Chemistry & Camera) instrument package consists of two remote sensing instruments:

- a) The first planetary science Laser-Induced Breakdown Spectrometer (LIBS)
- b) A remote Micro-Imager (RMI) (Wiens et al., 2013).

The LIBS provides elemental compositions, while the RMI places the LIBS analyses in their geomorphologic context. Both instruments will help determine which rock and soil material

are of sufficient interest to use the contact and analytical laboratory instruments for further characterization.

a) LIBS Instrument

The LIBS instrument uses a pulsed laser. The laser is focused onto a sample within 7 m of the rover. The LIBS instrument ablates atoms and ions in electronically excited states within a plasma from which they decay, producing light. The light is carried to three dispersive spectrometers that obtain spectra over a range of 240– 850 nm. The spectra consist of emission lines of elements present in samples.

b) Remote Micro-Imager (RMI)

The ChemCam instrument includes the highest resolution camera ever sent to the surface of Mars. The RMI can be used to look for physical alterations of a rock caused by the presence of water in the past (Fig. 1.9).

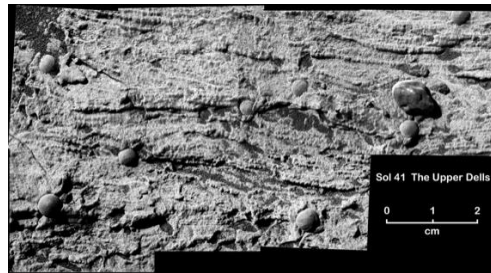


Figure 1.9. Microscopic Imager (MI) image on the Mars Exploration Rover (MER) of “festooning” on a Martian rock. Festooning is a trait of rock altered by water. Credit: NASA/JPL/Cornell/USGS

Several studies based on data obtained by the Curiosity rover from the Gale Crater were recently published. New data from ChemCam, were reported by Meslin et al., 2013. They explained the identification of two principal soil types. One main soil type is made of fine-grained particles, which carries a significant amount of hydrogen. This reflects the dust that covers the whole Martian surface. The other main soil type was coarse grained (up to 1 millimetre in size) and reflects the rocks that make up the Gale Crater. Meslin et al., (2013) have concluded that the ChemCam data did not reveal any significant exchange of water vapour between the regolith and the atmosphere.

Pathfinder, Spirit and Opportunity rovers had less sophisticated technology to analyse soil but their insights about the mineral composition of the Martian soil are similar to that reported by the Curiosity rover work. With ChemCam and Curiosity's other instruments, scientists are starting to obtain a deeper understanding of the composition and the geology history of the Martian soil.

1.6.2 ExoMars mission

Exobiologists have been studying data from past space missions in recent years trying to find any sign of present or past life on Mars. The discovery of some minerals such as clay and sulphates proves that there has been liquid water on the Martian surface during its early evolution. These discoveries make scientist more interested in studying the development of life forms and chemical reactions that could establish life. Hence, in 1999, a team of scientific advisors recommended to the European Space Agency (ESA) that it should pursue an exobiology mission using a rover that is able to access the subsurface in combination with the capability to perform experiments in an analytical laboratory. Therefore, ESA has established the ExoMars program to investigate the Martian environment and to demonstrate new technologies that pave the way for a Mars sample return mission in the future.

Currently the ExoMars concept has been modified in a way that two missions are expected within the ExoMars program: one consisting of an Orbiter plus an Entry, Descent and Landing Demonstrator Module, to be launched in 2016, and the other, featuring a rover, with a launch date in 2018 (Fig. 1.10) (Rull et al., 2011).

The initial design of the rover in (2006) had a weight of 240 kg and included 21 science instruments in addition to sample acquisition, preparation and handling systems. The scope of the science payload has been downsized several times and the rover mass was reduced to 150 kg with nine scientific instruments (Table 1.4). The rover will have the capability to travel on the Martian surface for a period of ~180 Martian sols. During this period it will cover a distance for several kilometres. This Pasteur package of instruments on the rover will carry out experiments to detect evidence of past and present life on samples from the surface and sub-surface. Mars is extremely cold and dry. It has a low atmospheric pressure (6-10 mbar) and all surface environments are subjected to very high levels of Ultra Violet (UV) and ionizing radiation. Consequently, the present surface of Mars is inhospitable for extant life as we know it and if life is still present on Mars, it would be in protective subsurface environments. Therefore, the rover will carry a drill to analyse the soil up to a depth of two metres below the Martian surface.



Figure 1.10. Elements of the ExoMars programme 2016-2018 Credit: ESA.

The initial design concept for a combined Raman and LIBS instrument for the ExoMars mission was first presented in 2006 at the International Conference on Space Optics. Since then, prototypes of the instrument were built, tested and developed (Ahlers et al., 2008). The main challenge was to combine the two techniques into a single instrument with the stringent mass, volume and the power requirements of the ExoMars mission. During the period from the initial design in 2006 until it was finished in 2009, ESA realised that the mission instrument such as the RLS instrument was too heavy and consumed too much power to be used for the mission. In an effort to reduce mass and costs, a new design had to be made that would include only the Raman spectroscopy instrument while the LIBS capability was left out of the ExoMars mission.

ESA has also confirmed that the mission would lose several of the initial planned instruments because of budget cuts. Instruments that were “de-scoped” from the ExoMars mission include:

- Mars X-Ray Diffractometer (Mars-XRD): This instrument retrieves information about the composition of crystalline minerals
- Miniaturised Mössbauer Spectrometer (MIMOS-II): This instrument provides the mineralogical composition of iron-bearing surface rocks, soils and sediments
- The Life Marker Chip: This instrument detects specific molecules associated with life
- Humboldt payload: This instrument was previously known as the GEP (Geophysical and Environmental) payload. It was designed to study atmospheric variations and the internal structure of the planet by monitoring Mars quakes (The ExoMars Newsletter, European Space Agency, 2012).

The remaining rover instruments for the ExoMars mission are listed in table 1.4.

PanCam	The Panoramic Camera: It will perform Digital Topographic Mapping of Mars.
WISDOM	Water Ice and Subsurface Deposit Observation On Mars, ground penetrating radar. WISDOM uses radar pulses, covering the frequency range from 500 MHz to 3 GHz, to map the subterranean.
CLUPI	Close - UP Imager: A camera system to obtain high-resolution colour close-up images.
Ma-MISS	Mars Multi-spectral Imager for Subsurface Studies: It will analyse the internal surface of the borehole generated by the ExoMars drill.
MicrOmega	A visible plus infrared imaging spectrometer: It will identify the mineralogical and the molecular composition of samples collected by the ExoMars drill.

Raman laser spectrometer	Raman spectrometer will determine the mineralogical composition of the soil and identify organic molecules.
MOMA	Mars Organic Molecule Analyser is a combined pyrolysis gas chromatograph mass spectrometer (GC-MS) and laser desorption mass spectrometer (LD-MS). It will study biomarkers to explain the potential origin, evolution and the distribution of life on Mars.
ISEM	Infrared Spectrometer for ExoMars: It will measure the mineralogical composition of a sample's surface. ISEM and PanCam contribute to the selection of suitable samples for further analysis by other instruments.
ADRON-RM	Adron is a neutron detector: It will search for hydrated minerals and subsurface water contributing to the search for suitable areas for drilling and sample collection.

Table 1.4. Onboard instruments for the ExoMars mission.

1.7 Conclusion

Mars has already revealed a great diversity of rocks at the surface. Recent missions such as Mars Express (ESA, 2003) and the Mars Reconnaissance Orbiters (NASA, 2005) have greatly extended our knowledge of the Martian surface through the discoveries of new minerals such as carbonates with the use of hyper spectral observations (Murchie et al., 2009). Morphological and mineralogical studies show that Mars could have experienced a major climate change in the past. It also revealed that the early conditions of Mars were warmer and wetter than today and could potentially have hosted life.

Each exploration mission focuses on more specific questions. Consequently, we can expect our understanding of the specific geologic environments and the evolution of Mars in general to continue to improve for the next decade. There is a need for more missions with new instruments such as a Raman spectrometer to better understand the changing geological environments and to analyse organic molecules. New missions such as the current Mars Curiosity rover and the planned ExoMars, will help to investigate the surface and subsurface of Mars and will provide a more accurate understanding of the (bio) geochemistry of the planetary surface. This PhD project will contribute in understanding the origin and evolution of geological environments on Mars in future missions such as the ExoMars mission. In these future missions, *in situ* measurements will help to detect carbonates and sulphates and the specific geological processes that led to their formation. The ExoMars mission is equipped

with a Raman spectrometer as an *in situ* instrument. This instrument is designed to provide more accurate *in situ* information compared to previous missions and the evaluation of the instrument undertaken in this thesis represents part of the large on-going work to better interpret the data hopefully obtained on Mars in the near future.

1.8 References

- Abell, P.A. et al., (2009), Scientific Exploration of Near-Earth Objects via the Orion Crew Exploration Vehicle, *Meteoritics & Planetary Science* 44, Nr 12, p. 1825-1836.
- Ahlers, B., I. Hutchinson, R. Ingley and Raman LIBS EBB team, (2008), Combined Raman/LIBS Spectrometer Elegant Breadboard - Built and Tested - and Flight Model Spectrometer Unit, *Proc. 7th Int. Conf. on Space Optics*, pp. 8.
- Baker, V. R. (1982), *The channels of Mars*, Research supported by NASA, NSF, and Australian-American Educational Foundation Austin, TX, University of Texas Press, pp. 198.
- Bandfield, J. L. et al., (2003), Spectroscopic Identification of Carbonate Minerals in the Martian Dust, *Science* 301, p. 1084-1087.
- Bibring, J. P. et al., (2006), Global mineralogical Aqueous Mars History Derived from OMEGA/Mars Express Data, *Science*, Vol. 312, p. 400-404.
- Bish, D. L. et al., (2013), X-ray Diffraction Results from Mars Science Laboratory: Mineralogy of Rocknest at Gale Crater, doi: 10.1126/science.1238932.
- Bogard, D. D. and D. H. Garrison, (1999), Argon-39-argon-40 "ages" and trapped argon in Martian shergottites, Chassigny, and Allan Hills 84001, *Meteorit. Planet. Sci.*, Vol. 34, p. 451-473.
- Bouvier, A., J. Blichert-Toft, and F. Albarède, (2009), Martian meteorite chronology and the evolution of the interior of Mars, *Earth and Planetary Science Letters*, Vol. 280, p. 285-295.
- Bouvier, A., J. Blichert-Toft, J. D. Vervoort, and F. Albarède, (2005), The age of the SNC meteorites and the antiquity of the Martian surface, *Earth and Planetary Science Letters*, Vol. 240, p. 221-233.
- Bridges, J. et al., (2001), Alteration assemblages in Martian meteorites: implications for near-surface processes. *Space Sci. Rev.* 96, p. 365-392.
- Carr, M. H. and J. W. Head, (2010), Geologic history of Mars, *Earth Planet. Earth and Planetary Science Letters* 294, p.185–203.
- Catling, D. C. (1999), A chemical model for evaporites on early Mars: Possible sedimentary tracers of the early climate and implications for exploration, *Journal of Geophysical Research*, Vol. 104, Issue E7, p. 16453-16470.
- Chyba, C. F., and C. B. Phillips, (2002), Europa as an Abode of Life, *Orig. Life Evol. Biosph.*, 32, p. 47-68.
- Edgett, K. S. et al., Curiosity's Mars Hand Lens Imager (MAHLI) Investigation. *Space Sci. Rev.* 170, 259–317, (2012). doi: 10.1007/s11214-012-9910-4.

- Ehlmann, et al., (2011), Subsurface water and clay mineral formation during the early history of Mars. *Nature* 79(7371), p. 53-60.
- Fairen, A. G. et al., (2004), Inhibition of carbonate synthesis in acidic oceans on early Mars. *Nature*, Vol. 431, p. 423-426.
- Golden, D. C. et al., (2001), A simple inorganic process for formation of carbonates, magnetite, and sulfides in Martian meteorite ALH84001. *Am Min.* 86, p. 370-375.
- Gooding, J. L. (1978), Chemical Weathering on Mars Thermodynamic Stabilities of Primary Minerals (and Their Alteration Products) from Mafic Igneous Rock, *Icarus*, Vol. 33, p.483-513.
- Grady, M. M. (2008), *Astrobiology of the Terrestrial Planes, with Emphasis on Mars*. In complete course in Astrobiology, eds Horneck, G. and P. Rettberg. (Wiley-VCH Verlag GmbH and Co. KGaA), p. 203-222.
- Greeley, R., and J. E. Guest, (1987), Geologic Map of the Eastern Equatorial Region of Mars, USGS Misc. Inv. Ser. Map I-1802B.
- Grotzinger, J. P. et al., (2012), Mars Science Laboratory Mission and Science, Investigation, *Space Sci Rev* 170: p. 5-56.
- Hartmann, W. K. (1970), Lunar cratering chronology. *Icarus* 13, p. 299-301.
- Hartmann, W. K. (1999), Martian cratering. VI. Crater count isochrons and evidence for recent volcanism from Mars Global Surveyor. *Meteorit. Planet. Sci.* 34, p. 167-177.
- Hartmann, W. K. (2005), Martian cratering. 8. Isochron refinement and the chronology of Mars. *Icarus* 174, p. 294-320.
- Hartmann, W. K. and G. Neukum, (2001), Cratering chronology and the evolution of Mars. *Space Sci. Rev.* 96, p. 165-194.
- Hegde, S. and L. Kaltenecker, (2013), Colours of Extreme Exo-Earth Environments *Astrobiology*. 13(1). p. 47-56.
- Houtkooper, J. M. and D. Schulze-Makuch, (2010), Do perchlorates have a role for Martian life? *Journal of Cosmology* 5, p. 930-939.
- Ivanov, B. A. (2001), Mars/Moon cratering rate ratio estimates. *Space Sci. Rev.* 96, p. 87-104.
- Kallenbach, J. G. and W.K. Hartmann, Editors, *Chronology and Evolution of Mars*, Kluwer, Dordrecht, p. 105-164.
- Kieffer, H. H., B. M. Jakosky, C. W. Snyder and M. S. Matthews (1992), In: *Mars, Tucson: University of Arizona Press*. pp. 384–385.

- Laan, E., W. Westrenen, A. Wielders, J. Heiligers, (2009), Moonshot: a combined Raman/LIBS instrument for lunar exploration, 40th Lunar and Planetary Science, doi:10.1117/12.825883.
- Lapen, T. J. et al., (2010), A Younger Age for ALH84001 and Its Geochemical Link to Shergottite Sources in Mars; *Science*, Vol. 328, p. 347-351.
- Levin, G. V., A. H. Heim, J. R. Clendenning and M. F. Thompson, (1962), "Gulliver" - A Quest for Life on Mars, *Science* 138, p. 114-121
- Lipps, J. H. et al., (2004), Astrobiology of Jupiter's Icy Moons (PDF). *Proc. SPIE* 5555: 10.doi:10.1117/12.560356.
- Mahaffy, P. R. et al., The Sample Analysis at Mars, Investigation and Instrument Suite. *Space Sci. Rev.* 170, 401–478 (2012). doi: 10.1007/s11214-012-9879-z.
- Malin, M. C. and K. S. Edgett, (2000), Evidence for recent groundwater seepage and surface runoff on Mars. *Science* 288(5475), p. 2330-2335.
- McKay, C. P. et al., (2008), The Possible Origin and Persistence of Life on Enceladus and Detection of Biomarkers in the Plume, *Astrobiology*, Vol. 8, No. 5.
- McKay, C. P., H. D. Smith, (2005), Possibilities for methanogenic life in liquid methane on the surface of Titan, *Icarus*, Vol.178, Issue 1, p. 274-276.
- McKay, D. S. et al., (1996), Search for past life on Mars: Possible relic biogenic activity in Martian meteorite ALH 84001, *Science*, Vol. 273, p. 924-930.
- Meslin et al., (2013), Soil Diversity and Hydration as Observed by ChemCam at Gale Crater, Mars, doi: 10.1126/science.1238670.
- Murchie, S. L. et al., (2009), A synthesis of Martian aqueous mineralogy after 1 Mars year of observations from the Mars Reconnaissance Orbiter, *Journal of Geophys.* doi: 10.1029/2009JE003342.
- Neukum, G. and B.A. Ivanov, (1994), Crater size distribution and impact probabilities on Earth from lunar, terrestrial-planet, and asteroid cratering data. In: *Hazards due to Comets and Asteroids*, (T. Gehrels, Ed.) Univ. Arizona Press, pp. 359-416.
- Neukum, G., B. A. Ivanov and W. K. Hartmann, (2001), Cratering records in the inner Solar System in relation to the lunar reference system. *Space Sci. Rev.* 96, p. 55-86.
- Nyquist, L. E. et al., (2001), Ages and geologic histories of Martian meteorites, Vol. 96, Issue 1-4, pp 105-164.
- Poulet, F. et al., (2005), Phyllosilicates on Mars and implications for early main climate. *Nature* 438(7068), p. 623-627.

- Pollack, J. B., R. M. Haberle, J. Schaeffer and H. Lee, (1990), Simulations of the general circulation of the Martian atmosphere 1. Polar processes. *Journal of Geophysical Research* 95: doi: 10.1029/89JB01430. issn: 0148-0227.
- Rull, F., (2011), ExoMars Raman laser spectrometer for Exomars doi:10.1117/12.896787.
- Rull, F., S. Maurice, E. Diaz and the RLS Team, (2012), Raman spectroscopy for the 2018 ExoMars mission, *EPSC Abstracts*, Vol. 7, p. 740.
- Reynolds, J., B. S. Weir and C. C. Cockerham, (1983), Estimation of the coancestry coefficient: Basis for a short-term genetic distance. *Genetics* 105: 767-779.
- Schulze-Makuch, D. and L. N. Irwin, (2004), *Life in the Universe: Expectations and Constraints*, Springer-Verlag, Berlin, pp. 172.
- Scott, D. H. and K. L. Tanaka, (1986), Geologic map of the western equatorial region of Mars, U.S. Geol. Surv. Misc. Invest., Map, I-1802-A.
- Sheehan, W., (1996), *The Planet Mars: A History of Observation and Discovery*, Tucson: University of Arizona Press, pp.270.
- Stöffler, D. and G. Ryder, (2001), Stratigraphy and isotope ages of the lunar geologic units: Chronological standard for the inner Solar System. *Space Sci. Rev.* 96, p. 9-54.
- Tanaka, K. L. (1986), The stratigraphy of Mars, *Journal of Geophys. Res.*, 91, p. 139-58.
- Tanaka, K. L., D. H. Scott and R. Greeley, (1992), in *Mars*, Kieffer H. H., B.M. Jakosky, C.W. Synder, and M.S. Matthews (eds.), University of Arizona Press, Tucson, pp. 354–382.
- Treiman, A. H. and E. J. Essene, (2011), Chemical composition of magnetite in Martian meteorite ALH 84001: Revised appraisal from thermochemistry of phases in Fe-Mg-C-O, *Geochimica et Cosmochimica Acta* 75, p. 5324-5335.
- Werner, S. C. (2005), *Major Aspects of the Chronostratigraphy and Geologic Evolutionary History of Mars*. PhD thesis, Freie Universitaet Berlin, p. 160.
- Wiens, R. C. et al., (2013), Pre-flight calibration and initial data processing for the ChemCam laser-induced breakdown spectroscopy instrument on the Mars Science Laboratory rover, *Spectrochimica Acta Part B: Atomic Spectroscopy*, doi:10.1016/j.