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Reviewing *in situ* analytical techniques used to research Martian geochemistry: From the Viking Project to the MMX future mission

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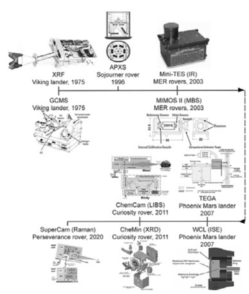
HIGHLIGHTS

- The evolution of *in situ* Martian analytical techniques.
- Elemental and molecular techniques provide key information about Mars surface.
- The Viking XRF and GCMS were the first *in situ* analytical techniques on Mars.
- Combination of analytical techniques provides better results.

GRAPHICAL ABSTRACT



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ABSTRACT

The study of space has always been a field of great interest and thus space missions are becoming more and more ambitious with time. Therefore, with the 50th anniversary of the first spacecraft to land on Mars, a review about how traditional analytical techniques have been adapted to the era of *in situ* space exploration is presented. From the Viking Project to the future MMX mission, the techniques used for the *in situ* study of the geochemistry of the Martian surface is described. These techniques have been differentiated according to the type of analysis: elemental and molecular. On the one hand, among the elemental analytical techniques the XRF, APXS, ISE and LIBS stand out. On the other hand, GCMS, TEGA, MBS, XRD, Raman and IR spectroscopy have been the molecular techniques used in the missions to Mars. Miniaturization, real-time measurements, automation, low power consumption and reliability of operation under extreme conditions are some of the major challenges that analytical chemistry has faced as a result of the technological and scientific requirements of space missions. In this way, this review gathers all the *in situ* analytical techniques that have reached the surface of Mars onboard landers or rovers with the aim of studying its geochemistry.

Contents

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1. Introduction

1.1. Historical background

Human beings have always been eager to learn about the objects seen in the sky during the nights. After a big effort and thanks to the advances in technologies developed in the 20th century, it was possible to send the first instruments, animals and then people into the outer space.

It was seen that with time space exploration has been using increasingly better technology to face increasingly more challenging goals. This desire to improve has allowed gaining a better understanding about planets, moons, galaxies, stars, asteroids, etc. In this way, it has been always an important aim of the space exploration to ascertain the geochemistry of celestial bodies. Geochemistry is the study of the chemistry of natural Earth and other rocky body materials and the chemical processes they are undergone to, both now and in the past [1]. Hence, by analyzing extraterrestrial material, information of early differentiation or the presence or absence of magnetic field and the plate tectonics can be determined and compared. In addition, as it is known that life could originate wherever appropriate conditions existed, the searching of water or sources of simple carbon-containing molecules is gaining more and more importance [2].

The main information about extraterrestrial geochemistry has been acquired by (1) analysis of returned samples from the Moon, (2) characterization of collected meteorites and planetary dust, and (3) studying some terrestrial analogs that are used to gain a better comprehension about the nature and geochemistry processes happened on Earth [3]. All these samples can be studied in the laboratory by analytical techniques. In fact, Aramendia et al.'s [4] review summarizes the most common analytical techniques used in order to study these samples. Nevertheless, there is a broad gap between the knowledge acquired from these samples and what is interpreted from remote planetary exploration. In this way, non-terrestrial samples found on the ground have undergone alteration processes, so the mineral phases found in these samples may not be the original or primary, but secondary ones or weathering products. Therefore, it is very important to study extraterrestrial material *in situ* so that the primary mineral phases can be described [5].

To characterize unaltered materials, two approaches have been used in space exploration. On the one hand, there are remote observations and on the other hand, *in situ* analyses with landed instruments. The spacecrafts that allow remote observations are orbiters, which are designed to travel to a distant celestial body and enter into orbit about it. After flyby spacecrafts, orbiters are among the first spacecrafts used to recognize and study celestial bodies. They cover large portions of planetary bodies, being able to map globally the composition of their surface. Besides, they can acquire high spatial and spectral resolution images and determine the abundance of different elements in the surface and subsurface, among other macroscopic capabilities [6].

In situ analyses with landed instruments include the use of lander and rover spacecrafts. Lander spacecrafts are designed to reach the surface of a celestial body and survive long enough to telemeter data back to Earth. Sometimes lander spacecrafts carry a rover inside them. Rover spacecraft are mobile robots, whose main purposes range from taking images and soils samples to collecting samples for return to Earth. Therefore, landers and rovers provide many *in situ* analyses on a micro scale.

As explained above, orbiters are used to carry out a first reconnaissance of the celestial body. Based on the remote observations, areas of interest or hotspots can be detected. In this way, possible landing zones for surface missions including analytical capabilities for *in situ* measurements (rovers or landers) are identified. Remote orbiters provide general information of big portions of terrains. In contrast, rover and lander observations provide more accurate information on a smaller scale. This feature provides scientific information of greater relevance.

In this way, it can be seen how the information provided by remote observations and surface measurements are complementary.

It should be noted that missions carrying on board analytical techniques must be tested prior to launch. Scientific instruments for planetary exploration missions are the results of years of avant-garde technological developments. Representative fields trials are therefore needed to evaluate and optimize their analytical performances. Thus, an increasing number of field trials are organized to gather insights about the potential scientific outcome of the scientific instruments that will serve, for example, to define the necessary hardware or software updates [7].

After the first orbiters, the Surveyor V mission, from the American Surveyor Program, became the first successful lander to carry an analytical measurement instrument for conducting experiments on the Moon's surface. On September 9, 1967 Surveyor V did the first *in situ* chemical analyses of the lunar surface [8]. Those analyses were performed by an alpha backscattering technique developed by professor Turkevich and his research team [9].

With the development of new technologies and the improvement of space missions, Soviets designed one of the great successes of the old Soviet's lunar exploration program, the Lunokhod 1 rover. It was the first robotic space exploration vehicle on the Moon's surface which carried more than one scientific instrument to accomplish experiments its surface. Lunokhod 1 was carried by the Luna 17 probe which landed on November 17, 1970 [10].

With the end of the space race between United States and the Soviet Union, missions to space became increasingly ambitious. Space agencies, such as the National Aeronautics and Space Administration (NASA), the Indian Space Research Organisation (ISRO), the European Space Agency (ESA), the China National Space Administration (CNSA), the Japan Exploration Agency (JAXA), Roscosmos, etc., started to collaborate with each other with a common goal in mind.

In this way, the first landers with scientific payloads to land on Mars were the Viking landers [11]. Subsequently, in 1997, the Sojourner Rover of the Mars Pathfinder Project became the first rover equipped with analytical instrumentation to land successfully on the Martian surface [12]. This review shows how rover and landers equipped with analytical techniques for the study *in situ* of the Martian surface have evolved over time.

1.2. Missions that studied the geochemistry of Mars by using in situ analytical techniques

There are several interesting fields to be studied on the surface of a celestial body, such as its geochemistry, its mineralogy and its astrobiology or exobiology. The term geochemistry has already been defined above. Mineralogy is concerned with the inorganic materials of the universe and, as such, is an essential component of the Earth and planetary science as almost every aspect of the Earth science involves minerals [13]. Astrobiology (earlier called exobiology or space biology) is the study of the chemistry, physics and adaptions that influence the origin, evolution and destiny of life [14]. Most of the Martian mission were, are and will be astrobiology focused, because detecting signs of potential extant life on Mars is challenging. The presence of organics on the red planet is expected to be very low and most likely linked to radiation-protected refuge and/or preservative strategies such as organo-mineral complexes [15]. The fact that few organic materials are expected on Mars makes biomineralization and the relationships between biomarkers, mineralogy and geochemistry key aspects of the search for extraterrestrial life. Thus, experiments are carried out on Earth using Martian analogs to study different scientific fields. For example, there are several studies on biomarkers and their relationship to mineralogy in the Icelandic hydrothermal system analog to Mars [15], in sulfate and iron oxide deposits in Río Tinto (Southwestern Spain) [16], among others. In addition to studies related to astrobiology, there is also information related to space-launched science instrumentation checks. The Rull et al.'s review [17] describes the analytical results gathered from the study of some of the most distinctive terrestrial analogs of Martian geological contexts, as well as lessons learned from the mission simulations performed at representative analog sites. Finally, there are laboratory and geochemical modeling experiments in which Mars conditions (pressure, temperature, humidity, etc.) are simulated and they can show how the minerals phases have been altered. In this way, planetary missions are supported with models such as those shown by the work of Madariaga et at [18]. which observes structural changes in the gypsum-syngenite-görgeyite system at different temperatures [19], among others.

Finally, after explaining the many fields being studied in relation to Mars exploration, this part of the review includes all missions that have reached the surface of Mars in order to study the geochemistry of the planet through analytical techniques.

1.2.1. The Viking project

NASA's Viking Project became the first American mission to land a spacecraft safely on the surface of Mars and to return images. This project consisted of two identical spacecraft missions, the Viking 1 and the Viking 2, whose main scientific goal was the search for life. Both spacecrafts contained a lander (Fig. 1 A) and an orbiter. Each orbiter-lander pair flew together and entered into Mar's orbit, the lander then separated and descended to the planet's surface.

Viking 1 was launched on August 20th, 1975 and went into orbit around Mars on June 19th, 1976. While Viking 2 was launched on September 9th, 1975 and was inserted into Mars' orbit on August 7th, 1976. The safe landing sites were finally selected while the spacecraft were in orbit. On the one hand, on July 20th, 1976 the Viking 1 Lander separated from the Orbiter and touched down at Chryse Planitia (22°N, 312°E). Chryse Planitia region is close to the terminus of three large channel systems (Ares Vallis, Tiu Vallis and Simud Vallis), which were considered to be primarily fluvial in origin and to have been modified by aeolian processes. That was the reason why Chryse Planitia was of scientific interest [11,20,21].

On the other hand, the Viking 2 Lander landed on September 3rd, 1976, at Utopia Planitia (48°N, 134°E), which is an impact basin located at the northwest of the volcanic province of Elysium Planitia and northeast of Arabia Terra. Utopia Planitia was chosen for examination due to the presence of a large number and variety of periglacial features [11,20,21].

The Viking project was planned to continue for 90 days after landing. Nevertheless, each mission operated far beyond its design lifetime. Viking Orbiter 2 was commanded off on July 25th, 1978; Viking Lander 2 on April 11th, 1980; Viking Orbiter 1 on August 7th, 1980 and Viking Orbiter 1 on November 11th, 1982 [21].

The orbiters' scientific equipment was made up of cameras, an infrared spectrometer for water vapor mapping (MAWD) and an infrared radiometer for thermal mapping (IRTM). Conversely, the landers were composed of different cameras, a thermal

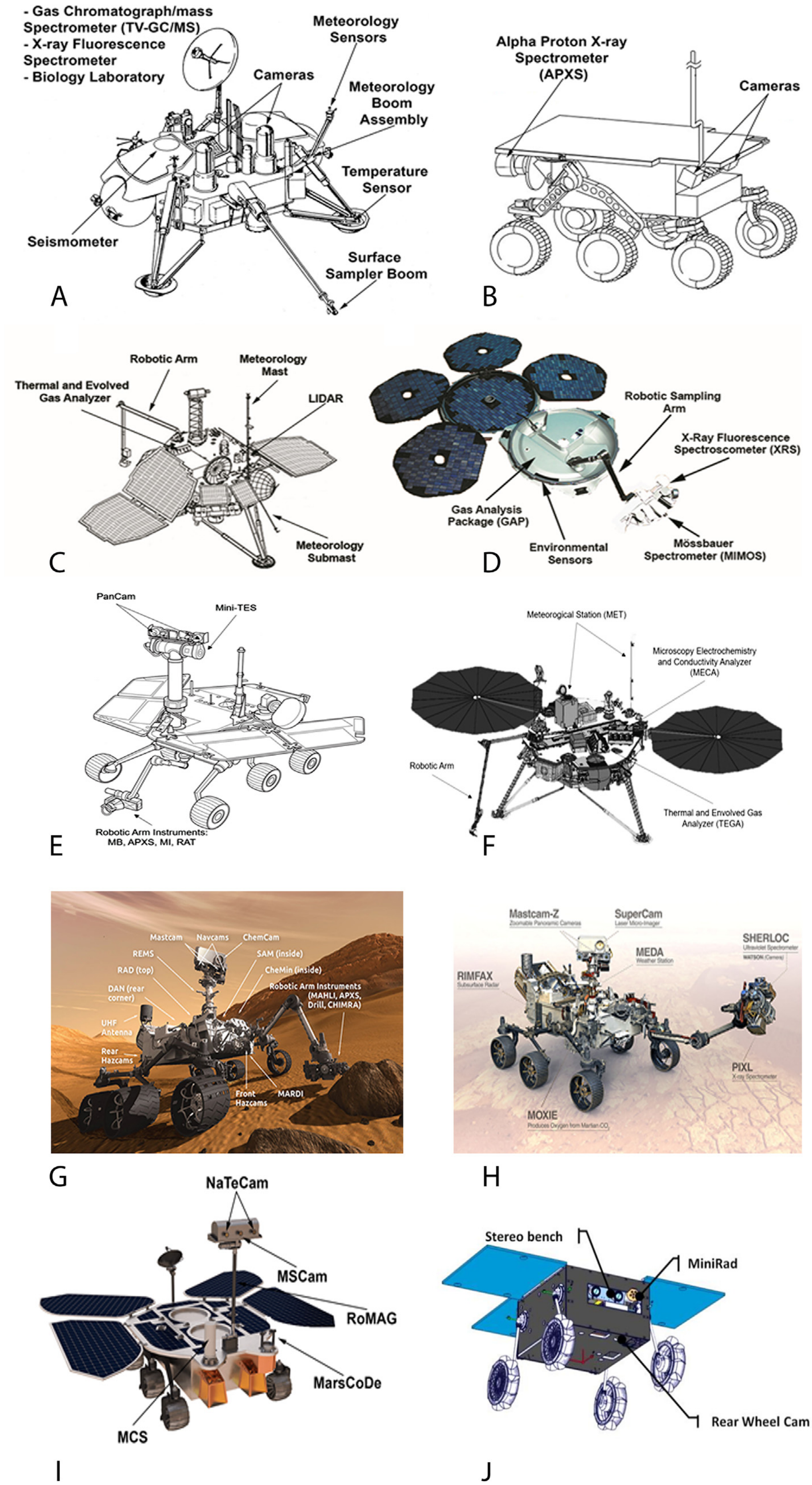


Fig. 1. *(A) Illustration of the Viking lander with its scientific payload shown. This figure has been edited from the original version* [69]. *(B) Illustration of the Mars Pathfinder's Sojourner rover with its APXS and some cameras shown. This figure has been edited from the original one* [70], *(C) Illustration of the Mars Polar lander with its scientific payload shown. This figure has been edited from the original one* [71], *(D) Illustration of the ESA's Beagle 2 lander instruments. This figure has been edited from the original version* [72], *(E) Illustration of the NASA's MER rovers with its analytical techniques shown. This figure has been edited from the original version* [73], *(F) Illustration of the Phoenix lander with its analytical techniques shown. This figure has been edited from the original version* [74], *(G) Illustration of the Curiosity rover with its scientific payload shown* [75], *(H) Illustration of the Perseverance rover with its analytical techniques shown* [76], *(I) Illustration of the Tianwen-1 rover with its scientific payload shown. This figure has been edited from the original version* [77], *and (J) Illustration of the MMX rover to Phobos* [68].

volatilization gas chromatograph/mass spectrometer (TV-GC/MS), a seismometer, an X-ray Fluorescence spectrometer (XRF), a weather instrument package (temperature, pressure, wind velocity), a remote sampler arm to take soil samples, and a biology laboratory with three different experiments. The three experiments were called pyrolytic release (PR), labeled release (LR), and gas exchange (GE) [22].

1.2.2. The Mars Pathfinder project — Sojourner rover and Carl Sagan memorial station lander

Mars Pathfinder, a spacecraft composed of a lander and a rover, was the first mission to explore in detail a landing area on Mars with a mobile platform. The lander was later named Carl Sagan Memorial Station in honor of the astronomer Dr. Carl Sagan, while the rover was called Sojourner. The Mars Pathfinder spacecraft was launched on December 4th, 1996 and landed on the Mars' Ares Vallis (19.33°N, 33.55°W, local reference frame) on July 4th, 1997 [12]. Although the mission was designed to operate between one week and one month, it worked around three months. Sojourner (Fig. 1 B), a rover weighing 10.5 kg and having 66 cm long, 48 cm wide and 30 cm tall, crossed over 100 m during its lifetime and extended the radius of investigations to a distance of approximately 12 m from the lander site [12,23]. As one of the objectives of this mission was to demonstrate a simple and low-cost system, the communications had to be improved, since two units, the rover and the landing spacecrafts had to work at the same time and send data to Earth. Thus in order to save rover power and mass, the rover communicated with Earth through the lander, requiring a short rover-lander communication range [24].

After many experiments, the lander battery degraded as expected during the first 30 days, so the spacecraft resulted in progressive cooling (night) and warming (day) cycles, until something in the telecommunications hardware failed due to the thermal stress. For this reason, the last communication with the main spacecraft was on October 7th, 1997 [25].

The Ares Vallis is a large channel that drained into the Chryse Planitia basin and that landscape is the result of ancient outflow channel formation and subsequent aeolian resurfacing of the depositional plain [26]. This landing site was selected because it appeared acceptably safe to land and permited the possibility to investigate a great variety of rock types deposited by catastrophic floods. Moreover, the Ares Vallis enabled to study different scientific questions, such as the differentiation of the crust, the development of weathering products, and the nature of the early Martian environment and its evolution [27].

The primary objective of the Pathfinder mission was to demonstrate a low-cost cruise, entry, descent, and landing system that could safely place a payload on the Martian surface. Moreover, other objectives were related to extend the scientific knowledge about the red planet. These included the study of the surface morphology and geology, the elemental composition of surface materials, a variety of atmospheric science investigations and rotational and orbital dynamics investigations.

To achieve the scientific goals, both rover and lander were equipped with different instruments. On the one hand, the Sojourner Rover carried an alpha proton X-ray spectrometer (APXS) and cameras. On the other hand, the lander carried (1) a spectroscopic imager (the Imager for Mars Pathfinder, IMP) composed of three cameras and (2) an Atmospheric Structure Instrument/Meteorology Package to measure the Martian atmosphere during the spacecraft descent, and to provide meteorology data both before and after landing [12].

1.2.3. Mars Surveyor 98 — Mars polar lander

The Mars Surveyor '98 project was a mission of the NASA's Mars Surveyor Program (MSP), which began in 1994 with plans to send spacecrafts to Mars every 26 months. The first spacecraft sent was the Mars Global Surveyor (MGS), a global mapping mission, which was launched in 1996 to orbit Mars. The next mission was the Mars Surveyor '98, which was comprised of two spacecrafts, the Mars Climate Orbiter, launched on December 11th, 1998, and the Mars Polar Lander (Fig. 1C), launched on January 3rd, 1999 [28,29]. Both the lander and the orbiter were designed to study the Martian weather, climate, and water and carbon dioxide budget of the Martian South Pole.

The orbiter carried a Pressure Modulated Infrared Radiometer (PMIRR) to collect data on the Martian climate and atmospheric/surface processes. Moreover, it also carried a multispectral camera (Mars Color Imager, MARCI) to perform remote sensing measurements using a wide angle and a medium angle cameras [30].

The lander carried a payload, including a robotic arm that deposited soil into a thermal evolved gas analyzer. In addition, the lander was equipped with a Light Detection and Ranging (LIDAR) instrument to measure atmospheric properties and detect sounds and a weather station similar to Pathfinder's, apart from a meteorology equipment [30].

Two small micro-landers, called Deep Space-2, were being carried as technology demonstrators. They were planned to plummet to the surface without parachutes, hoping to plunge into 2 m, leaving a radio on the surface to link with the MGS Orbiter. They were designed to send information about the regolith density, subsurface/surface temperature and pressure, and to capture a subsurface soil sample and analyze its water content [30].

The mission was expected to land in a region known as Planum Australe, due to the interest in studying the only known examples of extraterrestrial ice-sheets comparable to those of the Earth. Previous images received from the Viking and Mariner 9 orbiters allowed to select the landing site [31]. Unfortunately, the last contact with the vehicle was on December 3rd, 1999, when the spacecraft was to enter the atmosphere and the MGS tried to look for signs of the lander on the surface, but the search proved fruitless [28,29].

1.2.4. The Mars Express (MES) — the Beagle 2 lander

The space exploration mission Mars Express was the first planetary mission conducted by the ESA. MES was launched on June 2nd, 2003 and it included an orbiter, called the MES Orbiter, and a small lander. The lander was named Beagle 2 (Fig. 1 D), in honor of the ship involved in the epic voyage made by Charles Darwin and Robert FitzRoy during the years 1831 and 1836 that led to publish Darwin's "on the Origin of Species" book [32]. The landing site was selected after examining data from the instruments of the Mars Observer, MGS and the Viking Orbiters [33]. It is in the Isidis Planitia (11.6°N, 90.75°E), which is a large, flat sedimentary basin of impact origin straddling the relatively young northern plains and ancient southern highlands, where traces of life could have been preserved [34].

This mission supposes the first opportunity to study the mineralogy of Mars *in situ*. The MES Orbiter was captured into Mars orbit on December 25th, 2003 and it was equipped with instruments to make remote studies of the planet's subsurface, surface and atmosphere such as a High-Resolution Stereo Camera (HRSC), an IR-spectroimager (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité, OMEGA), a Mars Advanced Radar for Subsurface and Ionospheric Sounding (MARSIS), an imager of energetic neutral atoms with an analyzer of space plasmas (Analyzer of Space Plasmas Energetic Neutral Atoms, ASPERA-3), and a Mars Express Radio Science Experiment (MaRS) [35]. The orbiter was also equipped with spectrometers, such as an infrared spectrometer (Planetary Fourier Spectrometer, PES) and an ultraviolet spectrometer (Spectroscopy for the Investigation of the Characteristics of the Atmospheric of Mars, SPICAM). Orbital remote sensing observations, such as those made by OMEGA, enable a global characterization of Mars surface. Based on OMEGA operations, a first analysis of the global distribution of key mineral species at low and mid latitudes was performed [36]. That analysis revealed general trends of the distribution of surface material on Mars, broadly consistent with previous ground-based and space observations. Apart from many minerals detected such as pyroxene and olivine, among others, hydrated minerals have been detected in some spots, mostly within the ancient crust as also confirmed by further studies made by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instrument onboard the Mars Reconnaissance Orbiter [36,37]. Those analytical results have been used with scientific purposes and for choosing the landing site in several missions.

Although the Beagle 2 spacecraft successfully deployed from the Mars Express mother craft on December 19th, 2003, confirmation of a successful landing, six days later, was not forthcoming. Data from the lander were planned to be relayed back to Earth via the MES Orbiter and NASA's Mars Odyssey mission, but the mission only received data from the orbiter, which is still operating [33].

Twelve years later, on January 16th, 2015, ESA announced that the probe had been found in photos taken by the NASA's Mars Reconnaissance Orbiter. The lander was seen partially deployed on the surface, showing that the entry, descent and landing sequence worked and it did indeed successfully land on Mars on Christmas Day 2003, about 5 km from the center of its landing target [38].

The Beagle 2 was designed to perform a detailed geological, mineralogical and chemical analysis of the site's soils and rocks. For that reason, the Beagle 2 carried a Gas Analysis Package (GAP), the first Mössbauer spectrometer (MIMOS) to analyze the molecular composition of iron minerals and the X-ray fluorescence spectrometer (XRF) to characterize the elemental composition of the surface. Besides, it included environmental sensors, cameras (Marine), stereo cameras and a microscope, among others [32].

This lander was the most equipped one sent to Mars, aiming to fully characterize volatiles, soils and rocks around the landing site area. Unfortunatelly, something happened in the landing phase leaving a great human effort and instrumental developments without any returned data from the *in situ* analysis.

1.2.5. The Mars Exploration Rovers (MER) mission — Spirit and opportunity

The Mars Exploration Rovers (MER, Fig. 1 E) were part of the NASA's Mars Exploration Program, which by that time, had landed successfully three robots in Mars: the Viking 1 Lander, the Viking 2 Lander and the Sojourner Rover.

The MER mission had the primary objective of placing two mobile science laboratories on the surface of Mars in order to conduct *in situ* investigations for at least 90 sols (Martian days). In addition, the science goal of the MER mission was to determine the climatic, aqueous, and geologic history of a pair of sites on Mars where conditions may have been favorable to the preservation of pre-biotic or biotic processes evidences [39]. In this way, the MER-A Rover (called Spirit) and the MER-B (called Opportunity) were launched on June 10th, 2003, and July 7th, 2003, respectively.

Before landing, potential landing sites were mapped by using orbital images from Viking, MOC, and thermal emission imaging system (THEMIS) [40]. Finally, Spirit touched down on January 4th, 2004 on the volcanic plains of Gusev Crater, a place where mineral deposits suggested that Mars had a wet history [41].

Similar to the Gusev landing site, prelanding orbital images including those acquired by the Viking camera, the Odyssey THEMIS, and the MGS MOC were considered to select the Opportunity landing site [42]. Finally, Opportunity landed on January 24th, 2004 on Eagle Crater (Meridiani Planum), a possible former lake in a giant impact crater [43].

Even though both rovers were designed for completing 90 sols, Spirit and Opportunity exceeded their lifetime for many years. The Jet Propulsion Laboratory (JPL/NASA) lost contact with Spitit on March 22nd, 2010 and with Opportunity on March 10th, 2018 [39]. Despite the attempts of JPL to regain contact with both rovers, the missions were declared ended soon after confirming the lost of contact communications. The Spirit mission finished on March 22nd, 2010 and the Opportunity on February 13th, 2019.

Spirit and Opportunity were identical rovers equipped with the Athena Science Payload which was composed of a (1) Panoramic Camera (Pancam), (2) a Miniature Thermal Emission Spectrometer (Mini-TES), (3) Mösbauer Spectrometer (MB), (4) an APXS (5) a Magnet Array for collecting magnetic dust particles that were, afterwards, analyzed by MB and APXS, (6) a Microscopic Imager (MI) and (7) a Rock Abrasion Tool (RAT) [44].

1.2.6. The Mars Phoenix mission — Phoenix lander

The Phoenix mission was the first chosen for NASA's Scout Program. Its name is related with the mythological bird Phoenix. This is due to the fact that its intention to land on the Mars' pole after the failed attempt of the Mars Polar Lander.

The Mars Phoenix Lander (Fig. 1 F) was launched on August 4th, 2007, and landed on the northern plains of Mars on May 25th, 2008. The landing site was the Green Valley of Vastias Borealis (68.22°N, 125.7°W), in the Martian northern hemisphere. Thanks to the data from the High-Resolution Imaging Science Experiment (HiRISE) of the Mars Reconnaissance Orbiter, and from the Mars Orbiter Laser Altimeter (MOLA), Green Valley was selected as the Phoenix Lander landing site [45]. The arctic of Mars was selected to land because the primary goals were to study the history and current state of water in the Martian north polar region, and to understand if the landing site represented a habitable zone [46]. Phoenix completed its mission in August 2008, and made a last brief communication with Earth on November 2nd, 2008, as available solar power dropped with the Martian winter.

The lander was equiped with several instruments capable of characterizing the ice, including (1) a Robotic Arm, (2) a Microscopy, Electrochemistry and Conductivity Analyzer (MECA) that consisted of a wet chemistry lab (WCL) to extract soluble ions from the Martian soils, an optical and atomic force microscopes, and a thermal and electrical conductivity probe, (3) a Robotic Arm Camera, (4) a Surface Stereo Imager, (5) a Thermal and Evolved Gas Analyzer (TEGA), (6) a Mars Descent and (7) a Meteorological Station (MET) to record the daily weather of Mars [47].

1.2.7. The Mars Science Laboratory (MSL) mission — Curiosity rover

The MSL mission was launched on November 26th, 2011, and successfully delivered the rover Curiosity (Fig. 1 G) to the surface of Mars on August 5th, 2012. After having traveled more than 25 km, the Curiosity Rover remains active on Mars. Gale Crater was formed when a meteor hit Mars in its early history, about 3.5–3.8 billion years ago. As the meteor impact punched a hole in the terrain, it is probable that water was retained in the crater over its history. The selection of Curiosity's landing site was enabled by the remote sensing instruments onboard several orbital platforms, including MRO, which carries the Context Imager (CTX), the MiRISE and the CRISM instruments. CRISM was used to determine the minerals present at the surface, which helped to detect distinctive geologic units and asses the nature of past aqueous environment. MiRISE and CTX provided morphologic information regarding the minerals' stratigraphic context while also addressing landing site safety concerns [48].

In that way, NASA chose the Gale Crater, in the Aeolis Mensae region on the Southern edge of Elysium Planitia, as the landing site of the Curiosity Rover with the aim of assessing whether Mars ever had an environment capable of supporting microbial life [49]. The scientific goals were to determine whether life ever arose on Mars, to characterize the climate of Mars, to characterize its geology and to prepare for human exploration. In order to achieve those aims, the MSL Curiosity Rover was sent to Mars with a series of science sets, which are classified into contact, remote sensing, environmental, and analytical laboratory instruments.

Firstly, the two contact instruments onboard the Curiosity are the APXS and the Mars Hand Lens Imager (MAHLI). Secondly, the Chemical Camera (ChemCam) and the Mast Cameras (Mastcam) are the two remote sensing instruments of the rover to characterize the Martian surface. Thirdly, the environmental system of Curiosity is composed by the following instruments: (a) the Dynamic Albedo of Neutron (DAN), (b) the Mars Descent Imager (MARDI), (c) the Radiation Assessment Detector (RAD), (d) the Rover Environmental Monitoring Station (REMS), and (e) the Mars Science Laboratory Entry Descent and Landing Instrument (MEDLI). Finally, the analytical laboratory system is composed by the Chemistry and Mineralogy (CheMin) and the Sample Analysis at Mars (SAM) instruments [50].

At the time of writing this review (December 2021), Curiosity has successfully traversed along the Gale Crater for more than 3100 sols. The traverse of the rover was divided intro three main stratigraphic groups that were deposited following the formation of the crater in the late Noachian/early Hesperian. These groups were (1) the Bradbury Group, (2) the Mount (Mt.) Sharp Group, and (3) the Siccar Point Group.

The Bradbury Group is located on the crater floor from the base of Aeolis Palus and consists of predominately fluvially-deposited conglomerate and sandstone, associated with deposition during delta progradation and was sampled by the rover during sols 1–750.

The Mount Sharp Group encompasses the sedimentary units deposited as part of the original Mt. Sharp succession. This group is also named Murrau formation, which was analyzed from sol 755, and is largely finely-laminated mudstone interpreted to having been deposited within the standing water located at the end of Gale crater's ancient fluviolacustrine system.

The Siccar Point Group is a lithified aeolian capping unit that has been analyzed *in situ* from sol 990 to 1352 [51].

1.2.8. The insight mission — insight lander

The twelfth mission of NASA's Discovery Program was InSight (Interior Exploration using Seismic Investigations, Geodesy and Heat Transport). This lander launched on May 5th, 2018 and landed on November 26th, 2018 [52] in Elysium Planitia (4.502°N, 135.623°E) [53], in the vicinity of the Curiosity Rover landing site. Data gathered by orbiters (MRO, CTX and HiRISE) allowed a detailed characterization of the landing site [54]. The purpose of the InSight Lander was to perform the first comprehensive surface-based geophysical investigation of Mars. It was in order to help scientist answer key questions about the early formation of rocky planets in our inner Solar System (Mercury, Venus, Earth, and Mars), as well as rocky exoplanets. In this way, Elysium Planitia was not selected for its surface features, but for safety considerations.

The scientific goals of this mission were to understand the formation and evolution of terrestrial planets through investigation of the interior structure and processes of Mars and to determine its present level of tectonic activity and impact flux [55].

The InSight lander carried three instruments: (1) the Seismic Experiment for Interior Structure (SEIS), (2) the Heat Flow and Physical Properties Package (HP^3) and (3) the Rotation and Interior Structure Experiment (RISE) [56]. The lander is also equipped with an Auxiliary Payload Subsystem (APSS) to provide information about the weather and, nowadays, it is still sending to Earth reports about the weather and daily images.

1.2.9. The Mars 2020 mission — Perseverance rover

On July 30th, 2020, NASA launched the Perseverance Rover (Fig. 1H) of the Mars 2020 mission, which landed in the Jezero Crater, located on the western edge of Isidis Planitia, on February 18th, 2021 [57]. Recent high-resolution orbital imaging systems onboard MGS, Mars Odyssey, Mars Express, and the MRO have revolutioned the understanding of the Martian surface, and has led to an updated global geologic map of Mars and numerous local geologic mapping efforts identifying meter and sub-meter surface detail [58]. Hence thanks to that orbit data Jezero crater was selected to land as scientists believe that the area was once flooded with water and was home to ancient river delta [57].

The Mars 2020 mission is part of the NASA's Mars Exploration Program. One of its high-priority goals is to answer key questions about the potential for life on Mars. It is designed to address four overarching goals:

(1) The investigation of the mineralogy and geology of the Jezero Crater as representative of the ancient Martian environment.
(2) The assessment of the habitability of this ancient environment.
(3) The identification of rocks with a high potential of preserving biosignatures.
(4) The study of the current environmental Martian conditions in the preparation for human exploration.

The rover introduces a drill coupled to a catching system that will collect samples which could return to Earth in the future Mars Sample Return mission [59]. Besides, it is equipped with seven science instruments: (1) Mastcam-Z, (2) Mars Environmental Dynamics Analyzer (MEDA), (3) Mars Oxygen *In Situ* Resource Utilization Experiment (MOXIE), (4) Planetary Instrument for X-ray Lithochemistry (PIXL), (5) Radar Imager for Mars' Subsurface Experiment (RIMFAX), (6) Scanning Habitable Environments with Radar and Luminescence for Organics and Chemicals (SHERLOC) and (7) SuperCam [60,61].

1.2.10. The TIANWEN-1 mission — TIANWEN-1 rover

China's first Mars exploration mission, Tianwen-1, was launched on July 23rd, 2020, and entered into the Mars orbit on February 10, 2021. The selection of a candidate landing region for Tianwan-1's rover (Fig. 1 I) involved both engineering safety and scientific importance. Finally, based on orbiter data the selected site to land was Utopia Planitia, which is the largest recognized impact basin in the northern hemisphere of Mars, where the rover landed on May 15, 2021. The area is to the south of the NASA's Viking 2 Lander landing site and northwest of the spot where the NASA's InSight Lander touched down.

The main scientific objectives of Tianwen-1 are to study the characteristics of the Martian topography ang geological structure; to study the characteristics of the soil on the Martian surface and the distribution of water ice; to investigate the subsurface composition of the Martian surface; to study the ionosphere, surface climate and environmental characteristics of Mars and to study the Martian physical fields and internal structure [62].

To achieve those objectives, Tianwen-1 is equipped with thirteen scientific instruments, seven on the orbiter, six on the rover and two controllers separately installed on the orbiter and the rover, respectively. The scientific payload mounted on the rover includes: (1) Navigation and Terrain Camera (NaTeCam), (2) Multispectral Camera (MSCam), (3) Mars Rover Penetrating Radar

(RoPeR), (4) Mars Surface Composition Detector (MarsCoDe), (5) Mars Rover Magnetometer (RoMAG), and (6) Mars Climate Station (MCS).

1.2.11. The Exomars 2022 mission — Rosalind Frankiln rover

The Exobiology on Mars, or more commonly known as ExoMars 2022, mission will consist of a European rover, Rosalind Franklin, and a Russian surface platform, Kazachok. After a journey of nine months, the ExoMars rover will travel across the Martian surface to search for signs of life, collect samples with a drill and analyze them by *in situ* instruments and by other more sophisticated systems. These last ones will be installed in the Analytical Laboratory Drawer (ALD), a clean laboratory were the samples collected by the drill would be analyzed. The landing site selected is Oxia Planum, which is situated at the eastern margin of the Chryse basin at the outlet of the Coogoon Valles system [63]. Oxia Planum is a 200 km-wide low-relief terrain characterized by hydrous clay-bearing bedrock units. This region is of scientific interest as it exhibits at least two distinct aqueous environments, both of which occurred during the Noanchian: (1) a first phase that led to the deposition and alteration of 100 m of layered clay-rich deposits and (2) a second phase of a fluviodeltaic system that postdates the widespread clay-rich layered unit [64]. In this way, scientists are convinced that those sediments are ideally suited for the exobiology rover.

ExoMars 2022 will be the first mission to combine the capability to move across the surface and to study Mars at variable depths, from surface down to 2 m [65].

The rover is equipped with nine instruments: (1) Panoramic Camera (PanCam), (2) Infrared Spectrometer for ExoMars (ISEM), (3) Close-Up Imager (CLUPI), (4) Water Ice Subsurface Deposit Observation on Mars (WISDOM), (5) Autonomous Detector of Radiation of Neutrons Onboard Rover at Mars (ADRON-RM), (6) Mars Multispectral Imager for Subsurface Studies (Ma-MISS), and three more instruments installed in the ALD, (7) MicrOmega, (8) Raman Laser Spectrometer (RLS), and (9) Mars Organic Molecule Analyzer (MOMA).

1.2.12. The Martian Moons eXploration (MMX) mission

JAXA is planning to launch the MMX mission in 2024. MMX mission is a project to explore the Martian moons Phobos and Deimos [66]. Its major scientific goal is clarifying the origin of the two Martian moons and the evolution process of the Martian Sphere (Mars, Phobos and Deimos) [67].

The spacecraft will be inserted into Mars orbit in 2025, and will stay in the Martian area for about three years. It will perform scientific observation of Phobos from low altitudes and select sample collection sites. Then, the spacecraft will land on the surface of Phobos, perform *in situ* science with a small (about 25 Kg) rover (Fig. 1 J), collect samples, and return to Earth in 2029. Before entering the orbit to return to Earth, the spacecraft will carry out a flyby observation of Deimos [66].

The main probe has 7 science instruments: (1) the Telescopic Nadir imager for GeOmOrphology (TENGOO), (2) the Optical RadiOmeter composed of Chromatic Imagers (OROCHI), (3) a LIDAR to gather information on the shape of Phobos, (4) the MMX Infrared Spectrometer (MIRS), (5) the Mars-moon Exploration with Gamma Rays and Neutrons (MEGANE), (6) the Circum-Martian Dust Monitor (CMDM), and (7) the Mass Spectrum Analyzer (MSA) [67].

The MMX Rover is a contribution by the Centre National d'Etudes Spatiales (CNES) and the German Aerospace Center (DLR). It will be delivered to the surface of Phobos to perform *in situ* science but also to serve as a scout, preparing the landing of the main spacecraft. Its currently considered scientific payload consists of cameras, a Raman Spectrometer (RAX), and a thermal mapper (miniRAD) [68].

2. Objective

In situ analytical devices have gained popularity in the last years, especially due to some unique features such as portability, energy consumption, downsizing, real-time field measurements, automation, low-cost and easy-to-use. In the special case of space science, the need to bring measurement techniques marked a milestone in the history of Analytical Chemistry, as all its instrumentation had to be adapted to the new needs. Thus, bearing in mind that this year 2021 celebrates the 50th anniversary of the first spacecraft to achieve successfully a soft landing (Mars 3 lander) on Mars, the main objective of this review is to gather the analytical techniques that have been used to research *in situ* the geochemistry of Mars onboard landing spacecraft (rovers and landers).

3. The advancement of analytical techniques motivated by spatial exploration

Until today, 10 spacecraft have successfully landed on Mars with the aim of exploring the geochemistry of the planet. In addition, two more missions, each including a rover, are planned for the near future.

3.1. In situ analytical techniques to measure the elemental composition of the Martian surface

3.1.1. X-ray fluorescence (XRF)

As mentioned above, XRF spectroscopy is one of the most common non-invasive techniques used for elemental characterization of non-terrestrial techniques.

To date three robotic missions have been equipped with an XRF spectrometer: the Viking landers, the Beagle 2 lander and the Perseverance rover. In this way, the XRF onboard the Viking landers carried out the first *in situ* geochemical analyses of the Martian regolith.

Initially, the Viking mission's first objective was to study the exobiology of the planet, as it was the first exploratory journey to Mars. Subsequently, as it was decided to extend the scientific payload of the landers, a XRF spectrometer was added (Fig. 2 A). Unfortunately, as the spacecraft design was already firm, the XRF construction was limited, especially in size and configuration [78], which affected the quality of its results. Each fluorescence analyzer consisted of two pairs of gas proportional counters, with each pair adjacent to a single, sealed radioisotope source. The sources were ^{55}Fe and ^{109}Cd, emitting 5.9 keV and 22.2 keV x-rays, respectively [79]. As the analytical performance of the instrument was limited by the energy resolution of the gas proportional counters used for X-ray detection, its resolution was 1.2 keV at 5.9 keV (Mn Kα line), expressed as full width half maximum (FWHM) [80]. Besides, its live time was about 14400 s and the limit of detection (LOD) for Rb, Sr and Zr was 42, 42 and 57 μg/g, respectively [80]. In tests of analytical performance on unknown samples, the elements detected were measured with accuracies, which compared favorably with those obtained by wet-chemical methods. However, the accuracy improved with increasing atomic number.

Despite its limitations, the XRF of the Viking landers got interesting results. According to the element concentration results interpreted by Soffen et al. [11], the elemental composition of Chryse and Utopia sites were similar, but they were not so similar to terrestrial soils. The main elements detected by the Viking landers were silicon and iron (supposing the 89% of elements detected). Then, in less abundance, magnesium, sulfur, aluminum, calcium, titanium, chloride and potassium were identified in decreasing order, and finally, another 2% of other minor elements were also detected [81,82]. The elemental concentrations were combined to

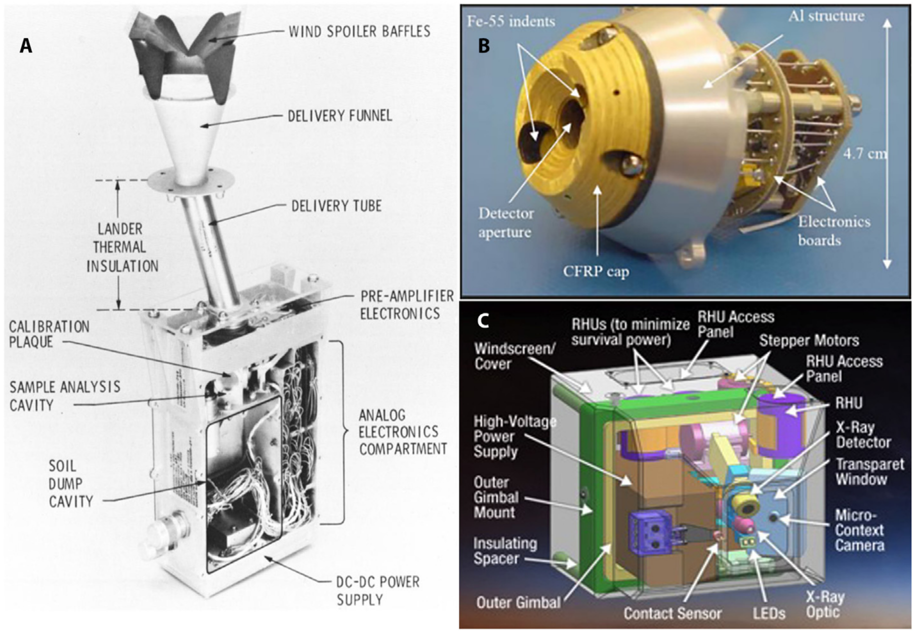


Fig. 2. *(A) Viking XRF instrument* [78], *(B) Beagle 2 spectrometer* [88] *and (C) PIXL arm mounted sensor head (Perseverance rover, Mars2020 mission)* [89].

simulate the presence of many types of geochemical compounds in the soils. In this way, there are many mineral models about the geochemistry of the Martian surface thanks to the data provided by Viking XRF [83,84].

Another XRF instrument was onboard the Beagle 2 lander (Fig. 2 B). Although the Beagle 2 lander failed, this instrument incorporated a number of innovative design features. In order to integrate the XRF device at the end of the robotic arm of the Beagle 2 lander, it had to be miniaturized. Its mass was about 0.156 Kg, the detector head assembly dimensions were 47 mm in diameter and 47 mm of length, and the dimensions of the signal processing electronics were 120 × 80 × 15 mm [80].

Most common XRF spectrometers use a dual source to illuminate the sample sequentially. However, the Beagle 2 XRF spectrometers was designed to used both types of sources simultaneously. The primary excitation was provided by two ^{55}Fe (105.6 MBq) sources (emitting Mn K X-rays of energy 5.9 keV and 6.5 keV) and two ^{109}Cd (8.77 MBq) sources (emitting Ag K X-rays of 22.2 keV and 24.9 keV) [80]. This improvement was developed in order to avoid the need of a source change mechanism that might have compromised the realible operation of the instrument and unnecessarily increased its mass.

The FWHM resolution of the flight spare Beagle 2 XRF device was about 0.39 KeV at Mn Kα [80]. Regarding to LODs of the Beagle 2 XRF, they were calculated to be 22, 27 and 26 μg/g for the trace elements Rb, Sr and Zr respectively, improving considerably those of Viking [80].

As has been described, the XRF of the Beagle 2 included improvements with respect to the Viking XRF for the study of the Martian surface geochemistry. Unfortunately, as the mission was unsuccessful, there are no real analytical results to compare with those obtained by the XRF of the Viking landers.

Subsequently to the Beagle 2 XRF, a very novel instrument was developed for the Curiosity rover payload. This was the initial CheMin, which combined X-ray diffraction with XRF. Both techniques aimed to study simultaneously mineralogy and geochemistry of the Martian surface. However, due to the fact that the landing site was warm, the CCD of the XRF was going to be warmer than expected. This fact was one of the reasons why the CheMin XRF requirement was drooped [85].

More than fifteen years after the second XRF on Mars onboard the Beagle 2 lander, the Perseverance rover of the Mars2020 mission has carried a much-improved version of this instrument to Mars. The XRF is called PIXL (Fig. 2C) and is mounted on the robotic arm of the rover. One of the most significant improvements of PIXL is that it can acquire high spectral resolution observations of rock and soil chemistry. Over a period of several hours, the instrument can autonomously raster-scan an area of the rock surface and acquire a hyperspectral map composed of several thousand of individual measured points. When correlated to visual image acquired by PIXL's camera, these maps reveal the distribution and abundance of chemical elements making up the rock. It weighs more than the other instruments previously shipped, 7.9 Kg and its FWHM spectral resolution at Mn Kα line is < 0.16 KeV [86].

On July 20, 2021 NASA published the first PIXL's chemical maps on its website [87]. These maps correspond to the elements: Na, Si, Cl, Ti, Fe, Mg, P, K, Cr, Ni, Al, S, Ca, Mn and Zn.

3.1.2. Alpha proton X-ray spectrometer (APXS)

The Rutherford alpha backscattering technique was invented to obtain *in situ*, for the first time, the chemical composition of the lunar surface material during the NASA's Surveyor mission in 1967–1968 [9]. After the success in analyzing the lunar surface, the backscattering spectroscopy technique became a common laboratory technique of chemical analyses. An instrument similar to that used to analyze the lunar surface, but substantially miniaturized and improved in its performance was used to obtain the chemical composition of Martian surface. This was the APXS and was used for the first time during the Pathfinder mission, onboard the Sojourner Rover. Subsequently, it was used by the Mars Exploration Rovers (MER) Spirit and Opportunity, and by the Curiosity rover.

The APXS is based on three different interactions of alpha particles from a radioactive source with matter: Rutherford backscattering (alpha mode), nuclear reactions of alpha particles with some light elements (proton mode), and generation of characteristic X-rays in the sample through ionization by alpha particles (X-ray mode). The alpha mode measures all elements heavier than helium; the x-ray mode measures all elements heavier than Na; and the proton mode obtains complementary data for elements in the transition regions, that is for Na, Mg, Si and Al. Combining these three modes it was possible to measure the abundances of all elements in the sample except for H and He [90]. Therefore, the geochemical information obtained by the APXS is more completed than that of XRF (elements lighter than Na are not detected).

The APXS of the Sojourner rover (Fig. 3 A) consisted of two parts: the sensor head and the electronics box. The electronics box was located inside the rover in a thermally controlled box and its dimensions were about 70 × 80 × 65 mm. The sensor head was mounted on the outside of the rover, with a diameter of 52 mm and a length of 65 mm [9]. In this way, the mobility of the rover enabled the instrument to access a wider variety of samples and make the first direct geochemical analyses of rocks. The overall weight was 0.55 Kg, and the power consumption came to only 0.4 W [91]. The detection limit of the measurements depended on the excitation mechanisms (alpha or X-ray), but in general, the LOD varied between 0.1 and 1 wt % depending on the element [91]. Most of the APXS data were obtained during the nights, when the surface temperature was usually between −50 °C and −90 °C and, therefore, the x-ray mode reached the best resolution [92]. The x-ray detector operated without any cooling and achieved an FWHM (5.9 keV) of about 250 eV. The Pathfinder APXS used about 40 mCi of ^{244}Cm alpha radioactive sources for its operation, and the source emitted a monochromatic beam of 5.8 MeV [92].

As both the Sojourner Rover and the Carl Sagan Memorial Station Lander were communicated to each other, the IMP provided the necessary multispectral images of the scene to select the APXS targets. In this way, the rover traversed in a clockwise direction around the lander to make its elemental measurements on the Martian rocks [25].

Many sampling sites, soils, and rocks around the lander were analyzed, such as the Barnacle Bill rock, which became the first rock ever analyzed on Mars (samples analyzed by the Viking Landers were just soils) [23]. Preliminary APXS results indicated that Si had the higher abundance in all the samples, followed by Fe, Al, Mg, Al, Ca, S, Na, Ti, Cl and K, in decreasing order [90]. These elemental results for the rock were similar to those of the soils in the sites measured by the Viking Landers. However, the soils measured by Sojourner had generally lower S and higher Cl abundance than the Viking ones. One of the greatest discoveries of the Pathfinder mission was the assumption of the fact that the surfaces of the rocks were covered by varying degrees of adhering dust or a weathering ring similar in composition to the dust. As the Martian soils had more S abundance than the rocks, the rocks probably were covered by a sulfur ring. This theory was proposed because the rock analyses contained appreciably more S than is normally accommodated in magmas or igneous rocks. Therefore, the different amounts of sulfur can come from weathering processes and from volcanic gases [90]. Nevertheless, the APXS method cannot discriminate between rock surface and adhering dust that was transported by the wind to rocks surfaces. Recalibrated and post normalized studies expose that there were also potassium, magnesium and chromium in the Martian samples [23]. Based on those elemental results, scientists suggested that the rocks analyzed by Pathfinder had an andesitic to basaltic composition, indicating a certain degree of differentiation from mantle-derived magmas [25].

However, as it happened with the elemental results of the Viking Landers, there are not any molecular results to confirm exactly the mineral phases present in the rocks and the soils. In this way, there are several scientific articles that speculate about possible minerals present in the Martian surface by combining APXS and IMP data [93].

A development of the Pathfinder APXS instrument was used on the two MERs. This technique was part of the Athena Payload (Fig. 3 B), which was mounted on the instrument deployment devices (IDD) of the two rovers. The high-resolution silicon drift detector was improved with an energy resolution of 160 eV at 5.9 keV [80]. The sensitivity of the instrument compared to the Pathfinder APXS was improved for the K lines of elements such as Ni, Zn and Br. This

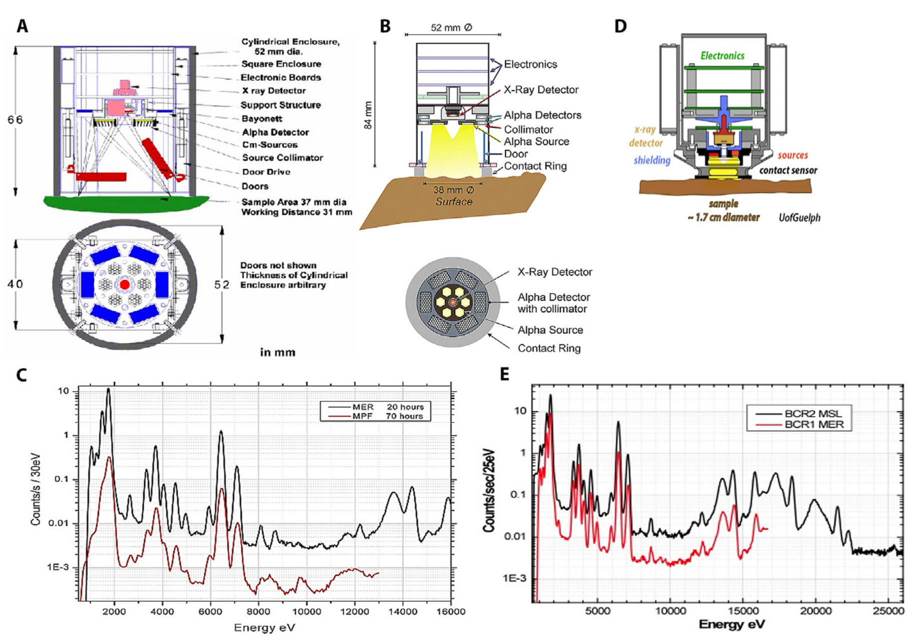


Fig. 3. *(A) APXS of the Mars Pathfinder Sojourner rover* [99], *(B) Athena APXS for the MERs, (C) X-ray spectra comparison between Athena APXS (MER, in black) and the Pathfinder APXS spare instrument (MPR, in red). Analyses were performed on the same sample (Andesite SSK1)* [100], *(D) APXS of the Curiosity rover* [101], *and (E) X-ray spectra comparison between MER (in red) and MSL (in black) APXS instruments on the same sample BCR reference material* [101]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

was because the APXS MER used 30 mm of distance between the sample and the detector to acquire the spectrum [94]. The temperature at which the best spectra resolution was achieved improved to approximately −40 °C [94]. The MER APXS used six ^{244}Cm sources, its global mass was about 0.37 Kg (almost half comparing the previous one), and the dimensions of the sensor head had 53 mm of diameter and 90 mm of length, whereas the dimensions of the electronics board were 170 × 100 × 10 mm^3 [80].

Fig. 3C shows the X-ray spectra comparison between Athena APXS (MER, in black) and the Pathfinder APXS spare instrument (MPF, in red). Analyses were performed on the same sample (andesite SSK1). The count rates increased by a factor of about 20 and the improvement of the energy resolution was best visible for the low elements Na to Si.

The first measurement with the Opportunity APXS was performed on a soil named Tarmac on the base of Eagle crater. This analytical technique detected in all the targets of Eagle crater Si, Fe, Al, Ca, Mg, Na, Ti, P, Cr, K, S, Cl, Mn, Ni, Z and Br, among others minor elements [95]. The elemental composition of the soils analyzed in Meridini Planum was similar to those mesaured by Spirit and Pathfiner.

The APXS results obtained by Spirit were almost similar to the Opportunity ones. However, the rocks of the Columbia Hills, a range of low hills inside Gusev crater, were chemically distinct from the primitive basalts in the plains. The APXS revealed the important alterations of the rocks in an aqueous and acid environment, because even after the abrasion of outcrops and rocks to a depth of 9 mm there was a high abundance of salts as indicated by the elevated levels of Br, Cl, and S [96]. In addition, when one of Spirit's front-wheel motors failed, the rover had to drive backward and drag along the stuck wheel, creating a shallow trenches. Due to this mishap, near Home Plate, the APXS detected pure silica in the trenches [97].

The following APXS to reach Mars was that of the Curiosity rover (Fig. 3 D), which was further improved. The temperature range spectra was extended upwards to approximately −5 °C, whereas the MER APXS was only capable to function below −40 °C [94]. The FWHM (5.9 keV) at low temperatures improved from ~ 155 eV to ~ 140 eV. In addition, the sensitivity (signal per second) was improved of an overall factor of 3, because the spectra was achieved by a closer proximity between the sample and the detector (~ 19 mm) [94]. The MSL APXS used 30 mCi conventional sealed ^{244}Cm sources in addition to the alpha emitting 30 mCi ^{244}Cm to further boost the light Z elements above Fe by a factor of 2. Another advancement was that the internal Peltier cooler of the SDD can be activated, delivering a cooling of the x-ray detector by −35 °C, extending the operation time with respect to the Martian day [94].

Jake_M, in the Bradbury Group, was the first rock analyzed by the Curiosity APXS instrument. This rock differed substantially in chemical composition from other known Martian igneous rocks, because it was alkaline (>15% normative nepheline) and relatively fractionated. Jake_M was compositionally similar to terrestrial mugearites, a rock type typically found in ocean islands and continental rifts. It could have been produced by extensive fractional crystalization of primary alkaline or transitional magma at elevated pressures, with or without elevated water contents. The discovery of Jake_M suggested that alkaline magmas may be more abundant on Mars than on Earth and that Curiosity could encounter even more fractionated alkaline rocks [98].

Fig. 3 E shows the X-ray spectra comparision between the MER and the MSL APXS instruments on the same sample BCR reference material. The MSL energy range has been extended to about 25 keV, where additional Compton and Rayleigh backscattered X-ray peaks can be identified. The overall sensitivity (signal per time) is increased by about a factor of 3 for low Z elements and about 6 for high Z elements above Ti due to added 30 mCi sealed Cm244 sources.

3.1.3. Ion selective electrode (ISE)

The Phoenix Mars lander included four chemistry cells, which were known as the Wet Chemistry Laboratories (WCLs). WCLs took part of the Microscopy Electrochemistry, and Conductivity Analyzer (MECA) package of the lander. WCLs were designed to address the aqueous chemistry and reactivity of the Martian surface material. By measuring a variety of dust and regolith properties including pH, redox potential, solution electrical conductivity and soluble ion species, it would be able to better understand Martian chemistry and mineralogy. Until then, there was no research on ionic strength or compounds formed when Martian soil mixed with water. However, this knowledge is critical, both to help to understand the biological potential of Mars and to assess hazards that may be encountered by future human explores. In this way, the MECA package included the first ISEs carried to the surface of Mars. WCL was designed to measure the concentration of the cations Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} and NH_4^{+}, and the anions Cl^{-}, Br^{-}, I^{-}, SO_4^{2-} and NO_3^{-}/ClO_4^{-} [102].

Perchlorate salts of calcium, magnesium- and sodium were detected *in situ* at the Pjoenix landing site by the MECA instrument [103]. Unfortunatelly, ISEs have never again been taken to the surface of Mars to carry out wet analytical chemistry analyses.

3.1.4. Laser-induced breakdown spectroscopy (LIBS)

APXS and XRF used abrasion tools (for example RAT in MER) to remove surface dust and analyze non-weathered material remotely. Later, another analytical instrument for analyzing clean samples remotely emerged, the LIBS instrument.

In this way, the ChemCam team of the Curiosity rover designed the first instrument with the capability to remotely clean and obtain depth profiles of samples by laser ablation. The ChemCam instrument combine the LIBS technique to provide elemental data, and a remote micro imager for context imaging the small LIBS points. In contrast to APXS and XRF, LIBS is a micro-destructive technique, so its use on labs has to be limited to samples that can be damaged. However, it offers several advantages in comparison with XRF and APXS. For example, LIBS allows characterizing quantitative elemental compositions including light elements like hydrogen and some other elements for which LIBS is uniquely sensitive (Li, Be, Rb, Sr, Ba, etc.). These abundances are measured from rasters of small observation points 350–550 μm in diameter [104].

All the different sections of ChemCam are mounted at the top of the rover's mast or in the rover body, and the overall weight of the instrument is almost 11 kg. The ChemCam LIBS was designed to obtain major element compositions for rocks and soils within 7 m of the instrument to relative accuracy of 10%. Its laser beam is invisible (1067 nm) and the LIBS spectrum covers a range from the deep ultraviolet to the infrared [104].

ChemCam helps to sample geological targets before using other instruments that require longer measurement times (contact XRF/APXS or mass spectrometry). The main differences with the elemental techniques exposed above in that ChemCam observations take approximately 6 min once the instrument is ready. In contrast, other techniques need to acquire, prepare, and then measure the samples. This process may takes severals sols. In addition, the Curiosity LIBS has very low LODs for certain elements, specifically the alkalis and alkaline earths. These LODs can be in the parts per million range [104].

ChemCam instrument has analyzed more than 2000 targets throughout the duration of the mission. Generally, ChemCam remote sensing data suggested that the Curiosity landing site was mostly composed by phyllosilicates, sulfates, hydrated sulfates, silica, carbonates and iron oxide minerals that were formed through some combination of fluvial, lacustrine, and aeolian processes [48]. For instance, the Yellowknife Bay was chemically basaltic but contained Mg-rich phyllosilicate (~ 20%), calcium sulfates (2–4%; anhydrite, bassanite) and a significant fraction of amorphous material (~ 30%).

The instruments of Curiosity are limited mostly to elemental composition rather than mineralogy. In order to fill this gap, the Perseverance rover is equipped with a remote mineral-identification instrument, the SuperCam instrument. SuperCam is a response to this requirement for remote mineralogy while preserving the ability ro remove dust prior to making observations of nearby targets, and providing the same or better chemistry and high-resolution imaging as ChemCam.

SuperCam is provided with a number of versatile remote-sensing techniques that can be used at long distance. These include LIBS, remote time-resolved Raman and luminiscence spectroscopies, and visible and infrared (VISIR) reflectance spectroscopy. As ChemCam, SuperCam is also equipped with a remote micro imager to high resolution color content imaging. Moreover, SuperCam includes also a microphone that can be used as a stand-alone tool for environmental studies or to determine physical properties of rocks and soils from the shocks of LIBS.

The Perseverance LIBS is able to detect and quantify the same elements than that of Curiosity, which are ~ 25, and performs analyses with the same distance capability than the Curiosity LIBS (~ 7 m) [105].

The laser used to achieve the plasmas provides up to 14 mJ and >10 MW/mm^2 of 1064 nm photons per pulse. And the pulsed laser, which is the same one as for Raman, frequency doubled to 532 nm [105]. The LOD is different for each element, but it is around 1000 ppm for alkalis and alkaline elements [105].

Perseverance LIBS has no significant analytical improvements over Curiosity LIBS. What has been improved is that the LIBS results are combined with those of the other SuperCam techniques for the same point analyzed, so that geochemistry and mineralogy are studied together. The first LIBS paper of the SuperCam instrument has been accepted bur does not yet have doi accessible.

The China's first Mars exploration mission also aims to study the Martian surface composition remotely, determining the geochemistry and the mineralogy. The MarSCoDe is a remote sensing instrument suite onboard the Tianwen-1 rover. This instrument includes a LIBS to provide elemental composition with a maximum distance of 7 m. For each LIBS measurement, the operation time of the MarSCoDe instrument ranges from 0.3 s to 4 min. The laser used is of 1064 nm, like the SuperCam one, and its spot is greater when the measurement is done at maximum distance of 7 m, being 0.25 mm. The LIBS spectral range goes from 240 to 850 nm approximately and the laser irradiance on the target with 23 mJ of energy and can soundly exceed 10 MW/mm^2 [106]. As it occurs with SuperCam, no analytical results have been published so far.

The MarSCoDe instrument includes as well as a Short Wave Infrared (SWIR) spectroscopy to conduct IR reflection analyses, and a telescopic micro imager to capture high resolution images of research targets at different distances.

Unlike the analytical techniques seen previously, LIBS has not been evolving over time. The most remarkable advance of this technique in Space Exploration is that it will be combined with others to simultaneously study the geochemistry and mineralogy remotely, providing the opportunity to perform collaborative scince and extract more information.

3.2. In situ analytical techniques to measure the molecular composition of the Martian surface

3.2.1. Gas chromatograph – mass spectrometer (GCMS)

GC has been one of the most frequently used *in situ* techniques for the chemical study of the atmospheres and surfaces of extraterrestrial bodies. This is because it offers great sensitivity and efficiency, is fast, requires low energy consumption, its format is robust, and it can be combined with spectrometric and spectroscopic devices, as well as with column instruments. GC coupled with mass spectroscopy (MS) is the most widely used methodology for the detection of organic matter. GC uses a thin capillary fiber known as column to separate different types of molecules, based on their chemical properties. Each type of molecule passes through the column at a different rate and the temperature of the column determines the rate of separation. Once processed by the GC, the molecules then enter into the mass spectrometer, which evaluates and identifies them by breaking each one into ionized fragments and detecting these fragments using their charge-to-mass ratio. This produced a unique profile of each compound that could be converted into a digital signal and could be transmitted to Earth [107].

So far, 4 spacecrafts equipped with a GC have traveled to Mars: the Viking landers, the Beagle 2 lander and the Curiosity rover. In the future, the Rosalind Franklin rover will also carry a GC in its scientific payload.

The Viking landers were equipped, for the first time ever, with a biology laboratory. This instrument was designed to carry out three different experiments in order to search for evidence of living microorganisms in material sampled form the Martian surface. These three experiments were called: the pyrolytic release (PR), the labeled release (LR) and the gas exchange (GEX). The PR had the capability to measure the fixation of carbon dioxide or carbon monoxide into organic matter. The LR experiment was designed to detect metabolic processes by monitoring the production of volatile carbon compounds from a radioactively labeled nutrient mixture. And the GEX monitored the gas exchanges in the head space above a soil sample which was either incubated in a humid environment or supplied with a rich organic nutrient solution [108]. The total mass of the biology laboratory was about 15.5 Kg, with a volume of 2.7 dm^3. It was designed to consume an average power of 12 W, but it could consume up to 180 W [108].

The changes in gas composition of the GEX were measured by GCMS (Fig. 4 A). This was the first time a GCMS has been taken into space. The Viking GCMS was designed to take a small soil sample, separate volatile elements using the GC, and analyze their composition with the MS. The GCMS permitted the release of volatile organic material by vaporization and finally thermal decomposition of more refractory substances through heating to various temperatures (50, 200, 350 and 500 °C) [109].

The GCMS was carefully designed to maximize performance while minimizing weight and power requirements. In this way, the instrument was composed by three tubular sample ovens that after filling with up to 100 mg of finely grounded (<300 μm) soil, they were tightly sealed into the gas line to assure quantitative transfer of the products. Moreover, the gas chromatographic column was specifically designed to tolerate water and carbon dioxide while transmitting a wide range of organic compounds. And, the electrically scanning magnetic sector mass spectrometer had a scan range from m/z 12 to 220 [109].

Each of the Viking landers analyzed two basaltic regolith samples using the TV-GC-MS with the goal of finding organic compounds. Both Viking landers detected chlorohydrocarbons, but these were thought to be terrestrial contamination from the solvents used to clean the instruments [110]. However, the Navarro-

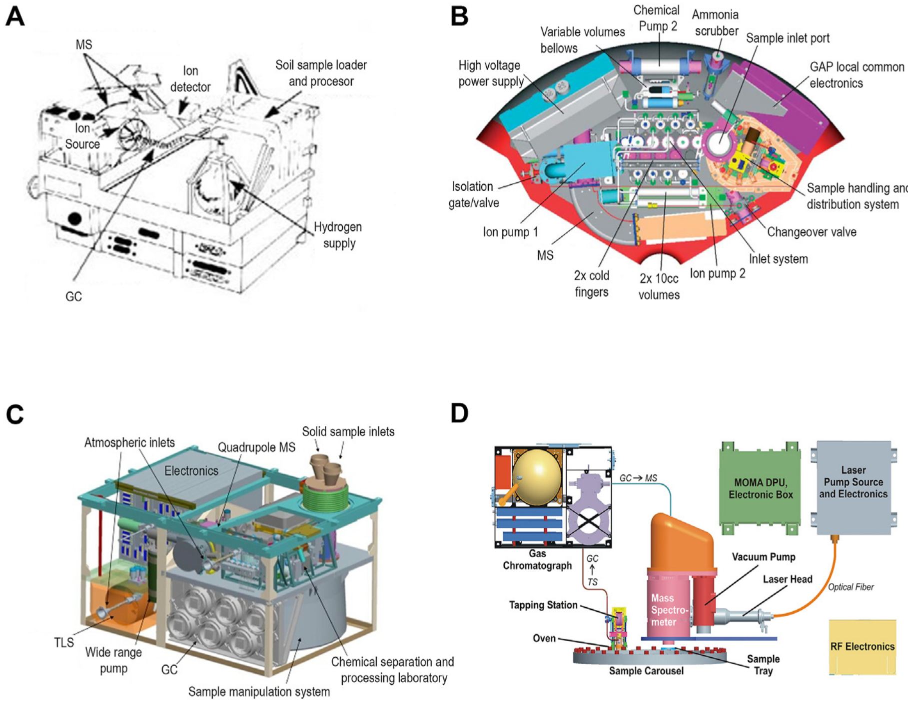


Fig. 4. *(A) Viking GCMS* [127], *(B) GAP instrument onboard the Beagle 2 lander* [88], *(C) SAM instrument of the Curiosity rover* [128] *and (D) MOMA instrument of the Rosalind Franklin rover* [129].

González et al. work demostrated that perchlorates could react with organics in sediment samples during heating, causing the release of CO_2 and formation of chlorohydrocarbons. The results from this work suggested that the chlorohydrocarbons detected by the Viking landers may have been the result of organic matter indigenous to the Martian soil reacting with perchlorates during sample heating [110].

Previously to the classification of Martian meteorites, significant abundances of trapped gasses such as argon, krypton, xenon, nitrogen and carbon dioxide were measured in shock-altered phases of the achondritic meteorite Elephant Moraine (EETA) 79001 from Antarctica. Surprisingly, the composition of this trapped gas resembled the Viking data for the Martian atmosphere [111,112]. The work of Treiman et al. shows the close similarity between trapped Shergotty, Nakhla, and Chassigny (SNC) meteorite gas and the Martian atmosphere [113]. In addition, the geohemistry of the SNCs matches that of Martian materials analyzed on Mars [113]. Therefore, Viking results allowed to appropriately classify SNCs meteorites found on Earth.

After Viking landers, the Beagle 2 lander was also equiped with a GCMS, which was part of the Gas Analysis Package (GAP) instrument (Fig. 4 B). GAP was designed to analyze samples of the Martian soil and atmosphere collected by the lander equipment, for evidence of chemical signatures of past biological processes. This instrument was located at the centre of the lander and had a total mass of 5.7 Kg, including electronics [88].

The GAP instrument had three modes of operation: quantitative analysis, qualitative analysis and precise isotopic measurement. GAP was designed to be fed either by direct atmospheric sampling or via one of the 12 ovens mounted on the carousel. The material acquired by the sampling tools, in the form of soil or rock, was deposited into one of the ovens, which was then rotated to a tapped station to be connected with the GAP. The ovens withstand temperatures up to 1000 °C [88].

In addition, the GAP instrument presented a great advantage over the GCMS of the Viking landers: it could operate in one or two ways, either analysing gases directly or from a solid sample producing appropriate analyte gases by chemical processing. In this way, GAP was very flexible, being able to investigate processes of atmospheric evolution, the nature of gases trapped in rocks and soils, low-temperature geochemistry, etc [88].

Regarding the MS, it was a 6 cm-radius magnetic sector spectrometer, which was designed to operate in both dynamic and static modes. It included six ion beam detectors. The main unit was a triple-collector array for the determination of N_2 (m/z 28, 29, 30), O_2 (m/z 32, 33, 34), and CO_2 (m/z 44, 45, 46). When operated dynamically, the MS should be able to measure stable isotope ratios to high degree of precision and accuracy. In contrast, static operation should allow high levels of sensitivity with some reduction in precision of the isotopic measurements [88].

As has been described, the GAP instrument included improvements with respect to the Viking GCMS. Unfortunately, as mentioned, there are no real analytical results.

The following GC to reach the Martian surface was onboard the Curiosity rover of the NASA's mission. In this case, a new and sophisticated instrument called the Sample Analysis at Mars (SAM) was designed (Fig. 4C). SAM addresses the chemical and isotopic composition of the atmosphere and volatiles extracted from solid samples. To do so, SAM combines three different techniques: the GC, the MS and the tunable laser spectroscopy (TLS). All of them provide complementary information on the same samples. The Curiosity rover's GCMS has a more novel design than previous landers equipped with a GCMS, since it also uses the capabilities of the TLS for the measure of methane, carbon dioxide and water vapor in the Martian atmosphere [114].

SAM is a 40 Kg instrument suite located in the interior of the rover. It is able to measure a suite of light isotopes and to analyze volatiles directly from the atmosphere or from solid samples. In addition to measurements of simple inorganic compounds and noble gases, SAM conduct a sensitive search for organic compounds with thermal or chemical extraction from sieved samples delivered by the sample processing system on the Curiosity rover's robotic arm [114].

The GC assembly contains six complementary chromatographic columns. The stationary phases of the columns are selected to provide a broad range of detection capability for both light and heavy organic molecules for a range of molecular polarity and for inorganic volatiles. The proportional integral differential heater circuit provided by the SAM electronics independently heats each column. Only one column is operated at a time and each column provides a signal independent of the mass spectrometer. The MS can detect the major species contained in the sample down to the part per million level, with a 10^5 dynamic linear range [114].

As samples of drilled rock or scooped soil are heated within SAM, components in them are vaporized and piped to the different instruments. The MS separates elements and compound by mass for identification and measurement. The GC separates the volatiles into various components for analysis. The TLS measures the abundance of various isotopes of carbon, hydrogen, and oxygen in atmospheric gases such as methane, water vapor, and carbon dioxide [115]. Many sources of organic compounds that SAM might detect could be exogenous, indigenous, or terrestrial contaminations because the exogenously sourced compounds are directly derived from in-fall meteorites, interplanetary dust particles and larger volatile-rich impactors such as comets or carbonaceous asteroids [114]. Fortunately, this instrument can differ isotopically between the possible biogenic or abiogenic origin of these compounds. Exogenous organic carbon is expected to share chemical characteristics of carbon-rich meteorites and interplanetary dust [116]. It is possible that abiotic photosynthesis and the presence of exogenous material occur in the current Mars. These events coat the planet's surface with small amounts of organic compound. Besides, abiotic photosynthesis could also generate methane, which would be detected by the TLS [116].

Although the SAM instrument was not designed for *in situ* molecular analyses of the organogeochemistry in the Martian surface, it is important to highlight that in all of the analyzed solid compounds SAM detected chlorinated organic compounds above the instrument background levels [117]. While some authors argued that the source of these compounds may originate from reactions between oxychlorines and terrestrial organic carbon present in the instrument background, others have demostrated that it is originated from indigenous organic carbon present in samples [117,118]. This finding provides again an evidence of the possible past habitability of Mars, as well as other evidence shown by the other rovers and landers described in this manuscript.

In addition, SAM detected volatiles (water, oxygen, sulfur dioxide, carbon dioxide, and chlorine) in interesting rocks such as Rocknest, which is in the Bradbury Group [119]. Samples of the Rocknest aeolian deposit were heated to 835 °C under helium flow and evolved gases analyzed by Curiosity's SAM instrument suite. H_2O, SO_2, CO_2, and O_2 were the major gases released. Deposition of fine-grained Fe or Mg carbonate was the likely source of much of the evolved CO_2. Evolved O_2 was coincident with the release of Cl found. This fact suggested that oxygen was produced from thermal decomposition of an oxychloride compound. Carbon isotopes indicated multiple carbon sources and several simple organic compounds were detected [120].

SAM has generated many results and not all of them could be included in this review. In this way, as a summary it can be said that: Organic molecules are the building blocks of life, and they were discovered on Mars after a long search by the SAM instrument in several samples drilled from Mount Sharp and the surrounding plains. The organic molecules found were chlorobenzene, chloromethane, dichloromethane, dimethylsulfide, thiophene, methylthiophene, dithiolane, dithiapentane, dithiolane, trihiane, propanethiol, diathiapentase, methyl-naphthalene, benzoic acid and benzothiophene, among others [121,122].

The SAM instrument has found Mars's present atmosphere to be enriched in the heavier forms (isotopes) of argon, carbon, and hydrogen. This indicates that Mars has lost much of its original atmosphere and reservoir of water [123–125].

As can be seen, the SAM instrument has proved to be the best performing GCMS in the history of gas chromatography on the Martian's surface. This is due to the fact that the Viking results are still being questioned and that the Beagle 2lander did not manage to operate on Mars.

Following the important results obtained by SAM and based on the objectives of the ExoMars mission, the future Rosalind Franklin rover will also be equipped with a GCMS. This combination will be part of the Mars Organic Molecule Analyser (MOMA) instrument (Fig. 4 D), which will be the largest instrument in the rover. This instrument will also include a Laser Desorption coupled to the MS (MOMA LDMS). On the one hand, GCMS will be used for volatile molecules characterization. Volatile compounds thermally evolved from solid samples in a pyrolysis oven will be separated by the GC and then analyzed individually with the MS. On the other hand, for non-volatile molecules, MOMA will use the LDMS. LDMS will produce gas-phase ions by high-intensity laser pulses applied directly to a crushed sample surface. These ions will be transferred into the MS and analyzed. Both modes of operation will use a common linear ion trap MS for detection and identification of molecular ions [126].

MOMA will achieve the ExoMars scientific objective to search for signs of past or present life on Mars. It will analyze a wide range of organic compounds that may be found in drill samples acquired up to 2 m below the Martian surface.

As can be seen, MOMA includes further advances over previous GCMS. The most remarkable one is that it will be able to detect non-volatile organic molecules thank to the LDMS.

3.2.2. Thermal and evolved gas analyzer (TEGA)

One of the main objectives of the Mars pole missions was to study the reservoirs and the behaviour of volatiles. In this way, the TEGA instrument was developed to meet this need, which was onboard the Mars Polar lander and onboard the Phoenix Mars Lander. TEGA is used to study the gas evolved from heated samples that undergone decomposition or desorption. It is always used together with other analytical methods such as MS, Fourier transform spectroscopy, GC, or optical *in situ* evolved gas analysis, among others. Although it was designed primarily to study the volatiles in the Martian atmosphere, it has been also used to analyze the reservoirs of water, CO_2 and some minerals, such as carbonates, in the Martian soils. As samples have to be heated, TEGA is considered as a destructive analytical technique and performs its analysis inside the body of the lander, so it does not have the advantage of working remotely.

The Mars Polar lander of the Mars Surveyor mission was the first spacecraft to deliver a TEGA (Fig. 5 A) to the Martian surface in order to measure the volatile content of the Martian soil at depth. Specifically, it was used to determine the water and carbon dioxide content, to identify other minerals and to detect oxidizing compounds in the soils.

The instrument was composed of three main components: the main electronics, which are located in the payload electronic box, the auxiliary electronics box, which is located close to the instrument to reduce noise, and the sensor head. The sensor head included (1) eight single use thermal analyzer modules to receive soil samples and perform differential scanning calorimetry (DSC) over the temperature range of Mars ambient to 950 °C; (2) a gas handling system to distribute and control carrier or calibration gas; (3) an oxygen sensor to detect evolved oxygen; and (4) a tunable diode laser spectrometer to determine the amount of water vapor and carbon dioxide evolved from the DSC ovens.

Each thermal analyzer had two identical ovens, one for the sample and one (empty) for a reference. A sample of soil from depth would have been acquired with a robotic arm and deposited into a hooper over the selected thermal analyzer. Then, the DSC would have controlled the first temperature that would have been ramped up and down around the freezing point to detect the abundance of water ice by the influence of ice's lantent heat on the power required to heat the sample. The sample would then have been heated up to 950 °C with nitrogen. Subsequently, the TEGA would have analyzed the evolved gases as the ovens were heated to provide knowledge of correlated gas release associated with the phase transitions. TEGA would have determined water and carbone dioxide contents via a high-resolution tunable diode laser absorption spectrometer. Mineral phase transformations would have been calorimetrically detected while evolution of absorbed water and decomposition products would have been carried to the oxygen sensor and finally into the high-resolution tunable diode spectrometer. This spectrometer would have enabled the quantitative determination of the volatile content of the sample, and may constrain the isotopic ratios of the evolved gases. The total mass of TEGA was of 5.71 Kg and its power requirements varied as a function of cambient temperature, the mode in which it is operating, and the temperature of the ovens. It ranged from 9.6 W with all the heaters off to a maximum of 78.0 W with all the heaters operating. Each TEGA experiment would have probably taken 2 days and samples would have been acquired from depths of up to 0.5 m with the robotic arm [130–132].

The combination of DSC and EGA was particularly powerful, since volatile release can be characterized in a correlated way by both components. Unfortunately, the last contact with the vehicle was when it was to enter into the Martian atmosphere, so it could not do any experiment.

The following spacecraft that included a TEGA instrument in its scientific payload was the Phoenix lander (Fig. 5 B). This one, unlike the Mars Polar lander, did operate on the Martian surface and obtained important results. This instrument was based on the Mars Polar Lander's TEGA, but included some improvements. The most notable improvement was that the Phoenix TEGA was a combination of high temperature furnace to heat the samples and a mass spectrometer to determine the amount of volatiles.

The instrument was composed of two main components: the electronics, which were located in the lower section of the EGA package, and the sensor head, which was located in the upper section of the EGA package and it contained the thermal analyzer and the MS. As in the previous TEGA, the thermal analyzer was a calorimeter with a set of eight small ovens. Each one was used once and accepted the sample delivered by the robotic arm. The operation process is exactly the same as for the previous TEGA. However, when the evolved gases were formed, they were transported to the MS by a carrier gas of high-purity nitrogen, which was used to measure the mass and concentrations of specific molecules and atoms in a sample. The MS was sensitive to detection levels on the order of 10 parts per billion, a level that may detect tiny quantities of organic molecules potentially existing in the ice and soil. The MS was a miniature magnetic sector instrument controlled by microprocessor-driven power supplies. One feature was the gas enrichment cell that increased the partial pressures of the noble gases in an atmosphere sample by removing all the active gases, carbon dioxide, and nitrogen, to improve the accuracy of their isotopic ratio measurements [133].

The total mass of the Phoenix TEGA instrument was the same of the other TEGA, but the average of power consumption was of 13 W, less than the other. Its dimensions were 24 × 23 × 18 cm [133].

In its work on Mars, TEGA indicated carbonate thermal decomposition at both low and high temperatures. The low temperature thermal decomposition was consistent with the presence of magnesite or siderite, their solid solution, or any combination of both. The high temperature thermal decomposition was consistent with calcite, dolomite, or ankerite, or any combination of those phases. Those carbonates could be there due to the inheritance of ejecta from the Vastitas Borealis and Scandia region, inherited from material deposited by eolian processes, or formed *in situ* at the site

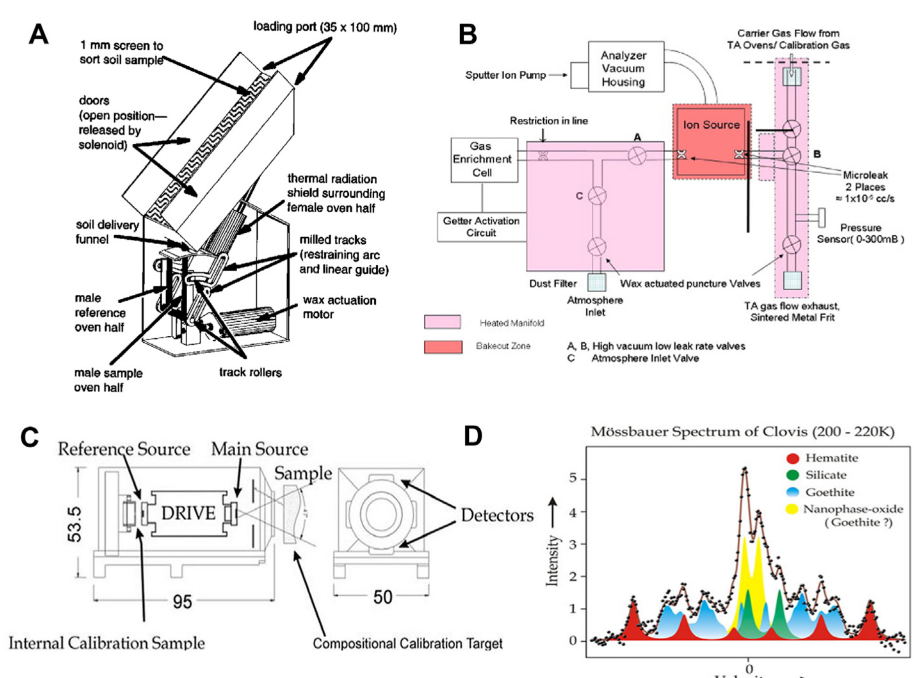


Fig. 5. *(A) Mars Polar TEGA* [132]*, (B) Phoenix lander TEGA* [133]*, (C) MIMOS II instrument* [143] *and (D) Mössbauer spectrum obtained by the MIMOS II instrument of the Spirit rover in the Clovis rock of Mars* [142].

where they were discovered. If this last option was the correct one, the soil would have had the suitable pH for microbial activity [134].

In order to predict salt precipitation sequences during freezing or evaporation of brines, equilibrium models were developed with data about soluble perchlorates, sulfates and carbonates in Martian soils. On the one hand, one of those models was proposed by Toner et al. [135]. They built a Pitzer model in the Na–K–Ca–Mg–Cl–SO_4–ClO_4–H_2O system at 298.15 K using compilations of solubility data in ternary and quaternary perchlorate systems. This model meant an improvement over the FREEZING CHEMISTRY (FREZCHEM), which was originally designed to stimulate salt chemistries and freezing processes at low temperatures (−45 to 25 °C) and 1 atm pressure [136]. Over the yearss, the FREZCHEM model has been broadened in order to explore cold biochemical processes on Earth, Mars, and Europa [136]. Both models, Pitzer and FREZCHEM, predicted the early precipitation of $KClO_4$, hydromagnesite ($3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and epsomite ($MgSO_4 \cdot 7H2O$), followed by dehydration of epsomite and gypsum to kieserite ($MgSO_4 \cdot H_2O$), and anhydrite ($CaSO_4$), respectively [137]. The Pitzer model predicted also that at low residual water contents the halite (NaCl), $NaClO_4 \cdot H_2O$, and $Mg(ClO_4)_2 \cdot 6H_2O$ would precipitate, whereas the FREZCHEM one predicts that halite and $NaClO_4 \cdot H_2O$ would never precipitate. According to the latter model, the salts found by the WCL instrument of the Phoenix Lander were not formed during evaporation near 298.15 K, but during possible freezing remains. Other models also predicted the freezing of calcite ($CaCO_3$), meridianiite ($MgSO_4 \cdot 11H_2O$), $MgCl_2 \cdot 12H_2O$, $NaClO_4 \cdot 2H_2O$, and $Mg(ClO_4)_2 \cdot 6H_2O$ at the eutectic (209 K) point [138].

3.2.3. Mössbauer spectroscopy (MBS)

Mössbauer spectroscopy is an extremely useful tool for quantitative analysis of Fe-bearing compounds and is therefore particulary used for *in situ* studies on the surface of Mars.

The Mössbauer effect provides information about the iron content of mineral samples by measurement of the Doppler shift in the velocity (or energy spectrum) of gamma-rays. These rays are emitted by a stationary target bombarded by an isotopically equivalent gamma-ray source. The absorption characteristics of the atoms give different spectra depending on their valence state and bonding. The signal strength is quantifiable, so the instrument can characterize the mineralogical composition of the rocks and soils. Its ability to measure valence states provides important information about oxidation and a detailed understanding of the weathering environment [139].

MBS leaves a footprint on the sample (in the order of cm). This technique is temperature sensitive and a Mössbauer spectra may change drastically with temperature. This fact helps in determining the nature of the Fe-bearing phases. Therefore, Mössbauer measurements are performed at different temperatures, including both the highest (during the day) and the lowest (during the night) temperatures [139]. Besides, the MB spectrometers that are built with backscatter measurement geometry require no sample preparation, a factor important for *in situ* planetary measurements.

So far, the Beagle 2 lander and the two MER rovers were equipped with a MBS. MB's results were helpful to interpret the results of other techniques, such as APXS or XRF and vice versa.

MIMOS II (Fig. 5C) was the miniaturized MBS developed for the two MER rovers. The MER MBS wa split into two parts: the detector head, which was mounted on a robotic arm, and the printed circuit board, which had the circuitry for the instrument control, data adquisition and storage, and was located in the rover's warm electronics box. The detector head was composed by the ^{57}Co radiation source and shielding, velocity transducer, and silicon PIN diode radiation detector. The total weight of the MIMOS II was about 500 g (400 g for the detector head and 100 g for the printed circuit board) and the dimensions of the instrument were about 90 × 50 × 40 mm for the sensor head, and 160 × 100 × 25 mm fot the electronic board. The power consumption was in the order of 2 W. The instrument was fully tested over the expected temperature range, which was from −120 to 40 °C for the sensor head, and from −50 to 40 °C for the electronics board [140].

The MIMOS II measurements were done by placing the detector head against the rock or soil in order to minimize possible microphonic noise on the velocity-modulated energy of the emitted gamma-rays. The field of view of the instrument was of 1.5 cm of diameter and the average information depth was 200–300 μm, assuming basaltic rock composition. The source intensity of about 300 mCi at launched gave a 6–12 h of time for adquisition a standard MB spectrum on Mars, depending on the total Fe content and which Fe-bearing phases were present [140].

The Opportunity MBS revealed four iron-bearing targets at Eagle crater: jarosite and hematite rich outcrop, hematite rich soil, olivine-bearing basaltic soil, and pyroxene-bearing basaltic rock [141].

The Spirit MBS identified eight Fe-bearing phases: olivine, pyroxene, ilmenite, magnetite, nanophase ferric oxide, hematite, goethite and a Fe^{3+} sulfate. It was seen that the Fe^{2+} from olivine and pyroxene was higher in moderately altered materials than in pervasively ones. Besides, MIMOS II allowed to detect the highest abundance of ilmenite and hematite in the less altered rocks. In contrast, goethite was found specially in Clovis, one of the most altered rocks. Goethite is a mineralogical evidence for aqueous processes because it has structural hydroxide and it is formed under aqueous conditions. Fig. 5 D represents the Mössbauer spectrum of the Clovis rock, in which appears the following minerals: hematite, silicate, geothite and a nanophase-oxide. Finally, regarding the results provided by MIMOS II, it was seen that every soil measured in Columbia Hills had a high concentration of iron sulfate and magnetite [41,142].

The Beagle 2 MBS was also divided into two parts, the detector head assembly and the electronics. The detector head assembly was located on the body of the rover and contained the radioactive sources, whereas the electronics were located at the base of the arms in the relatively warmer environment of the lander base. Its total weight was 541 g (438 g for the detector head and 102 g for the electronics) and the dimensions of the instrument were about 90 × 50 × 45 mm for the detection head, and 160 × 100 × 30 mm fot the electronics. The weight and the dimensions of this MBS are quite similar to those of the MIMOS II. The total consumption was 3 W, more than MIMOS II. Besides, the instrument was designed to use gamma-rays from the decay of ^{57}Co to ^{57}Fe. The footprint of the instrument was to be circular, with a diameter of about 1.5 cm, like MIMOS II, and the average information depth was of the order 100–200 mm, greater than MIMOS II [139].

Unfortunately, as the Mars Express mission was unsuccessful, the Beagle 2 MBS did not make any measurement and there are no real analytical results to compare with those obtained by the MBS of the MER rovers.

3.2.4. X-ray diffraction (XRD)

XRF, APXS and LIBS chemical data have been collected *in situ* by robotic spacecraft. These highly successful experiments provided critical constraints on the understanding of surface processes and planetary evolution. However, the mineralogy remained unknown. In this way, the MSL mission considered to incorporate simultaneous X-ray diffraction (XRD) instrument with XRF capabilities in order to analyze the mineralogy and the elemental composition of the Martian soils. This instrument was called CheMin (Fig. 6 A).

CheMin is located inside the main body of the rover, with a total mass of 10 Kg, dimensions of 30 × 30 × 30 cm and a power consumption of 40 W. This instrument returns quantitative powder X-ray diffraction data (XRD) from scooped soil and rock samples, delivered to it by the Sample Analysis/Sample Processing and Handling (SA/SPaH) and Collection and Handling for *In Situ* Martian Rock Analysis (CHIMRA) systems. Samples of 45–65 mm^3 from material sieved to <150 μm are delivered through a funnel to one of the 27 reusable cells arrayed on a sample wheel (Fig. 6 B). The sample cells are comprised of 8 mm diameter discs with 7 μm thick Mylar or Kapton windows spaced 170 μm apart. Within this volume, the sample is shaken by piezoelectric vibration a sonic frequency, causing the powder to flow past a narrow, collimated x-ray bean in random orientations over the course of an analysis. In this way, diffraction patterns exhibiting little to no preferred orientations can be obtained even from minerals normally exhibiting strong preferred orientation such as phyllosilicates [85,144].

During an analysis, a collimated X-ray beam from a micro focus X-ray tube source (Co anode and produces X-radiation from a 50 μm diameter spot) is directed through powdered or crushed sample material. Then, an x-ray sensitive CCD imager is positioned on the opposite side of the sample from the source and directly detects X-ray diffracted by the sample. The tube is normally operated at 28 KeV with a filament current of 1.5 A and cathode output of 100 μA. The detector is an E2V CCD-244 X-ray sensitive 600 × 600 pixel imager. Each CheMin analysis can take up to 10 h of time over two or more Martian nights. For typical well-ordered minerals, CheMin has a LOD of <3% by mass, an accuracy of better than 15% and a precision of better than 10% of the amount present for phases that are in a concentration higher than 12% [85,144].

CheMin has analyzed more than 19 drilled and 3 scooped samples to date, providing a wealth of mineralogical information. Fig. 6C shows the Curiosity traverse including the drilling points. To date, the major basaltic minerals identified by CheMin include Mg–Fe-olivines, Mg–Fe–Ca-pyroxenes, and Na–Ca–K-feldspars, while minor primary minerals include magnetite and ilmenite. CheMin also identified secondary minerals formed during alteration of the basalts, such as calcium sulfates (anhydrite and bassanite), iron oxides (hematite and akaganeite), pyrrhotite, clays and quartz. These secondary minerals form and persist only in limited ranges of temperature, pressure, and environment chemical conditions, and provide clues about the habitability of Mars [145].

3.2.5. Raman spectroscopy

Although it is an old-known technique, the benefits of using Raman spectroscopy for the laboratory study of mineralogy and organic compounds present in precious geologic samples has been widely recognized in recent years. This technique allows to analyse samples without destroying them, as it is a non-destructive technique. Moreover, as its portability is also well established in the scientific community, it has become the new key technique to be included in the scientific payload of the current and future rovers for space surface analysis. These are the Perseverance, the Rosalind Franklin and the MMX rovers.

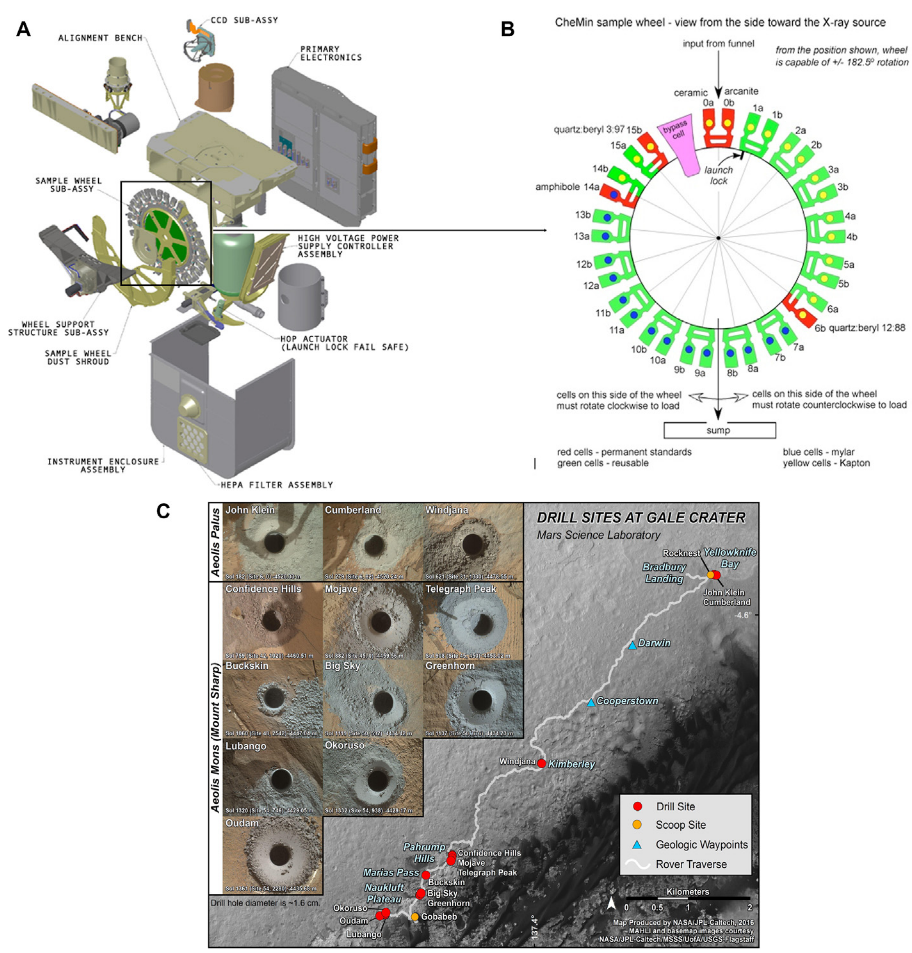


Fig. 6. *(A) CheMin XRD instrument, (B) CheMin sample wheel* [85] *and (C) Curiosity traverse including the drilling points* [146].

The Perseverance rover is equipped with two Raman spectrometers located in different instruments: SuperCam, which focuses on general mineral detection with some organic capabilities, and SHERLOC, which focuses on organics with some mineral capabilities.

The SHERLOC instrument (Fig. 7 A) combines imaging with ultraviolet (UV) resonance Raman and native deep UV fluorescence spectroscopy in order to identify potential biosignatures and understand the aqueous history of the Jezero region, the landing site of the Perseverance rover. This instrument is located in the arm of the rover and its total mass is of 6.85 Kg [147].

The spectrometer uses a 248.6 nm deep UV laser. This laser generates characteristic Raman and fluorescence photons from the Martian surface within the 100 μm laser spot and with a resolution of 0.31 nm. The laser is con-boresighted to the Autofocusing Contextual Imager (ACI) to facilitate a raster scan across the surface and to produce a chemical and organic maps of the sample. These spectral maps reveal more information than a single spectra by itself by relating minerals and chemicals to textures in a way simple bulk analysis does not. The Raman range goes from 810 to 4000 cm^{-1}, whereas the fluorescence range goes from 274 to 354 nm. The SHERLOC instrument is designed to detect the bulk organics with a sensitivity of 10^{-5} to 10^{-6} w/w over and 7 × 7 mm spot. Whereas, the fine scale organics should be detected with a sensitivity of 10^{-2} to 10^{-4} w/w spatially resolved at <100 μm. Finally, the organics and astrobiologically relevant minerals should be detected and classified to <100 μm resolution [147]. SHEROC is capable of correlating detected classes of organics with morphology (widths and shapes) to determine whether morphological candidates for microfossils, filaments, or stromatolitic layering are potentially biogenic (Fig. 7 A) [148].

As mentioned above, the SuperCam instrument of the Perseverance rover is equipped with the first remote time-resolved Raman and luminiscence spectrometer in space. Remote Time-Resolved Raman spectrocopy requires the use of a telescope, a pulsed laser, and a time-gated, intensified detector to provide sufficient signal to noise (Fig. 7 B). The intensified signal is projected in the form of multiple spectral traces onto a single CCD to maximize the product of spectral range and resolution. Moreover, a high-voltage power supply capable of operating in the Mars environment has been miniaturized, so that it mounts directly beneath the spectrometer [149,150].

The SuperCam Raman can analyze the sample from a measurement distance of 2–7 m with its visible laser (532 nm), which laser spot size can reach several mm in diameter. Its FWHM is of 12 cm^{-1} and the Raman range goes from 150 to 4400 cm^{-1}, due to the fact that 0-150 cm^{-1} range is cut by filters blocking the Rayleigh-scattered laser light. The total mass of the SuperCam instrument is about 10.4 Kg, including the mast unit, the body unit and the calibration targets. This is a higher weight than SHERLOC, but it should be noted that SuperCam includes Raman, LIBS and IR spectroscopies [149,150].

The two Mars 2020 Raman spectrometers are fundamentally different. While SuperCam avoids most fluorescence interferences to the Raman signal by time gating, SHERLOC avoids these interferences by operating in the deep UV where fluorescence does not occur. The SHERLOC spectral window starts at 810 cm^{-1}, missing most silicate structural signatures, which are the compound SuperCam focuses on.

The Rosalind Franklind rover will be also equipped with a Raman Laser Spectrometer. The RLS (Fig. 7C) will provide geological and mineralogical information on igneous, metamorpchic, and sedimentary processes, especially regarding water-related interactions. In addition, RLS can contribute to the tactical aspects of exploration by providing a quick assessment of organic content before the analysis with MOMA.

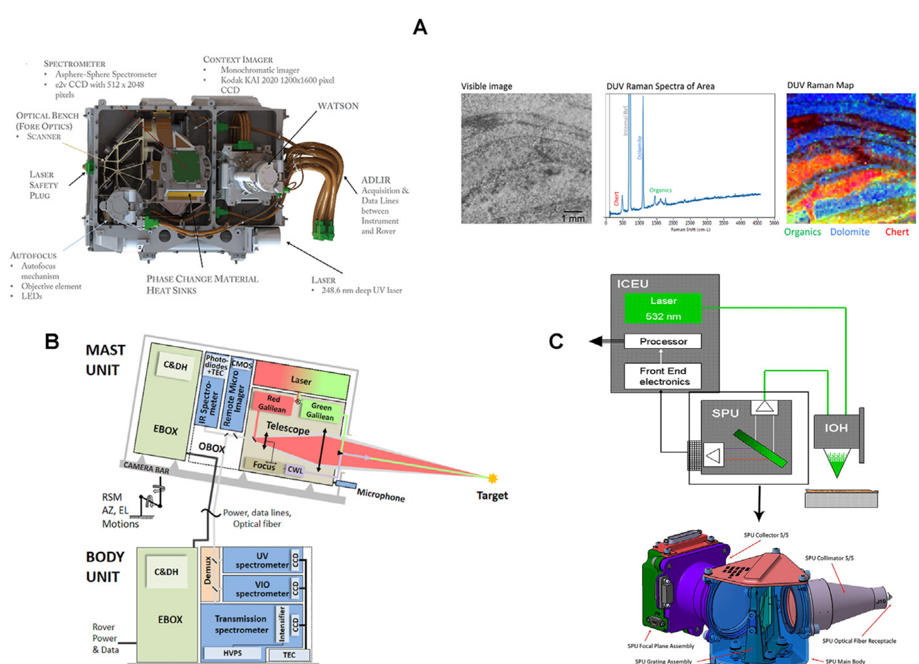


Fig. 7. *(A) Major SHERLOC assemblies* [155] *and an example of SHERLOC science* via *analysis of a Strelley Pool Formation Stromatolite sample using the laboratory breadboard MOBIUS instrument. The chert signature observed is highly attenuated by the edge filter but is observable in this sample. Color blend in the map and organics are green and yellow as they are mixed with the chert signature* [148]*; (B) Schematic diagram showing the major units and subcomponents of the SuperCam instrument suite* [105]*; and (C) RLS functional flow and the spectrometric unit flight model design (main body transparent)* [156]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The RLS instrument will be composed by the spectrometer unit, the optical head unit, and the electronic control unit, which also will include the laser excitation source. This Raman spectrometer will use a continuous excitation laser of 532 nm with a spot size of 50 μm. Its spectral range will go from 150 to 3800 cm^{-1} with a Raman resolution between 6 and 8 cm^{-1} in the fingerprint spectral region. To reduce noise and improve the scientific performance, the CCD will operate in the range −10 to −40 °C. This temperature will be guaranteed by a current-controlled thermoelectric cooler system that will be placed in contact with the detector [151–153].

In contrast to SuperCam, which performs the measurements remotely and without any sample preparation, RLS will work on the inside the rover's analytical laboratory drawer. The samples will be collected on the surface and subsurface (down to 2 m) with the ExoMars rover drill. Then, a rock crusher will reduce the sample to particulate matter that will be deposited in a small, refillable contaninder. Finally, a carousel will place the refillable containder under the Raman spectrometer for measuring the powdered samples. The total mass of the RLS instrument is about 2.4 Kg, a lower weight than the previous Raman instruments. Depending on the temperature, its power consumption will be between 20 and 30 W [151–153].

The last rover to carry a Raman spectrometer into space, specifically to the Martian Phobos moon, will be the MMX rover and the spectrometer is so-called as RAX. RAX will investigate the mineralogy of the Phobos surface. Besides, RAX will be a very compact, low-mass Raman instrument with a volume of approximately 81 × 98 × 125 mm and a mass of less than 1.4 Kg. The RAX instrument will consist of two physically separated units: the RAX laser assembly and the RAX spectrometer module. It will be located in the internal module of the rover and it will perform Raman spectroscopic measurements at a working distance of approximately 8 cm with a 532 nm excitation laser (50 μm in diameter). The laser will be designed for an optical output power of about 30 mW in the thermal operating range of +20 to +30 °C, but it can reach up to 100 mW. Since the laser linewidth will define the resolving power of the instrument, the laser temperature will be stabilized during RAX operations to an accuracy of ± 0.1 K by a thermoelectric module. Its spectral range will reach up 4000 cm^{-1} with a resolution of 10 cm^{-1}. In order to perform *in situ* measurements at different locations on Phobos, RAX will have an integrated autofocus mechanism, which will be used for precisely focusing of the laser beam onto the ground below the rover. Morever, in order to avoid the influence of ambient lights, the measurements of the RAX instrument will be performed during Phobos nights [154].

So far there are no scientific results from Raman spectroscopy on the soils and rocks of Mars or Phobos, due to the fact that this technique is novel in the study of mineralogy *in situ* outside the Earth. What is clear is that it is a very useful technique to characterize the mineralogy of very precious samples because it is a non-destructive analytica technique.

3.2.6. Infrared (IR) spectroscopy

Visible to near IR spectroscopy has been used from Mars orbit for nearly two decades. However, these spectrometers provide large-scale infrared information and generate large-scale images. Regarding surface located analysis, the MER rovers, the Curiosity rover, the Perseverance rover, the Tianwen-1 rover, the Rosalind Franklin rover and the MMX rover were, are and will be equipped with an infrared spectrometer. Unlike the IR spectrometers of the orbiters, the rover ones are point spectrometers and are designed to analyze the mineralogy of the Martian soils and rocks on a much smaller scale, so more detailed information can be obtained.

The first IR spectrometer reaching the surface of Mars was the Miniature Thermal Emission Spectrometer (Mini-TES) of the MER rovers. Mini-TES was a miniaturized version of the Mars Global Surveyor TES, which was used to map the mineral composition of the Martian surface by scanning the thermal emissions. In this case, Mini-TES measured the different spectrums of IR light, or heat, emitted from different minerals in rocks and soils. It was a Fourier Transform Spectrometer (FTS) that covered the spectral range from 5000 to 29000 nm (339.50–1997.06 cm^{-1}) and had a spectral resolution of 10 cm^{-1} [157].

Almost all of the Mini-TES instrumentation was located in the body of the rover at the bottom of the rover neck, its dimensions were 24 × 16 × 16 cm with a total mass of 2.4 Kg and its power consumption ranged from 0.3 W (daily average) to 5.6 W (operating). Unlike other instruments, Mini-TES possessed an uncooled detector (Deuterated Triglycine Sulfate, DTGS), which substantially reduced the complexity of its fabrication, and reached the scientific requirements for investigations. Its telescope was a compact 6.35 cm diameter Cassegrain telescope with an intermediate stop before the afocal section that provided excellent stray light rejection and efficient baffling. The instrument operational temperature range went from −10 to 30 °C and the diurnal variation of temperature on the surface of Mars excluded night operation when the temperature is too low [157].

The scene around the rover was imaged by Mini-TES at two different spatial scales, creating 3-dimension hyperspectral image cubes. These remote mineralogical measurements, together with the morphologic and color data from the Pancam, were used to direct the rover to specific targets of interest for detailed study by the full suite of the rover instruments. The mineralogical mappings of Mini-TES met these three requirements: (1) radiometric accuracy and precision necessary to uniquely determine the mineral abundances in mixtures to within 5% absolute relative presence, (2) spectral resolution sufficient to uniquely determine the mineral abundances in mixtures to within 5% relative presence, and (3) spatial resolution ≤ 25 cm at 10 m of distance necessary to resolve and identify individual rocks 0.5 m in size or larger in the rover near field [157,158].

The Mini-TES results of the Opportunity rover confirmed the presence of sulfates, hematite, glasses, oxides, feldspar, olivine and pyroxene in all the analyzed targets. The bands of the sulfates infrared spectra were decomposed in order to identify the mixture of sulfates the Martian samples were composed by. In this way, it was suggested that gypsum [$CaSO_4 \cdot 2H_2O$], bassanite [$CaSO_4 \cdot 1/2H_2O$], epsomite [$MgSO_4 \cdot 7H_2O$], kieserite [$MgSO_4 \cdot H_2O$], glauberite [$Na_2Ca(SO_4)_2$], and jarosite [$KFe_3(SO_4) \cdot 2(OH)_6$] could be part of Martian soils [159].

On the other hand, the mini-TES observations of the Spirit rover discovered a pure silica spectrum. This fact was one of the strongest evidence for concluding that Mars was much wetter than it was on the moment of the measurements, since the processes that could lead to such a concentrated silica require the presence of water [97]. Moreover, the Mini-TES indicated that rocks of Gusev crater were olivine-rich basalts with varying degrees of dust and other coatings. The soils were principally composed of pyroxene, sodic to intermediate plagioclase and andolvine. However, undisturbed soil spectra showed evidence for minor carbonates and bound water, being the Mg-carbonate the mineral which most fitted with the spectra. Combining the results of all the instruments, it could be concluded that rocks and soils of Gusev crater had a similar composition and that the soils were primarily formed from mechanically abraded ground and then mixed with materials coming from other sources such as any aqueous-altered materials [160]. As the Opportunity found, the coatings analyzed by Spirit were related to sulfates, specially with Mg and Ca-sulfates and even Fe-sulfates [161].

It is also considered a suitable technique for gas analyses as the majority of gaseous chemical substances possess their fundamental vibrational absorption bands in the mid-IR spectral region (2000–10000 nm). Moreover, small planetary instruments are not well suited to low abundance of H_2O and confuse H_2O, NH_3 and CH_4 isotopic species that overlap in mass number. For this reason, the SAM instrument of the Curiosity rover includes a tunable laser spectrometer (TLS) [162].

The TLS of the Curiosity is based on IR laser absorption within a multipass sample cell to record ultra-high resolution (0.0005 cm^{-1}) spectra of selected tunes of targeted species. The method is very sensitive (parts per million or parts per trillion), direct, non-destructive, easy to calibrate and unambiguous in species identification and isotopic ratio determinations without interference [114].

In this way, TLS complements the measurements of the MS and focuses on specific measurements for which it offers increased precision. The combination of GCMS with TLS makes the SAM instrument of the Curiosity rover the instrument with the most significant findings. In order to achieve the objectives of the TLS, two semiconductor continuous-wave laser sources scan over three wavelength regions chosen to target gas abundances and isotopic ratios. These are a near-infrared (NIR) tunable diode laser at 2.78 μm for carbon dioxide and water, and an interband-cascade (IC) laser at 3.27 μm for methane [114].

As has already indicated in the GCMS part, the SAM instrument has a total mass of 40 Kg. This is much heavier than the Mini-TES instrument, as it includes the GCMS. In addition, although Mini-TES had good resolution, it made measurements remotely on a larger scale than TLS, which makes measurements on small grains.

The TLS within the SAM instrument detected a seasonally varying background level of atmospheric methane and observed a ten-fold increase in methane over two-month period. This discovery could suggest that the methane can be produced by living organisms or by chemical reactions between rock and water [163].

The following IR spectrometer reaching the Martian surface has been that in the Perseverance rover. This technique is part of the SuperCam instrument, which together with LIBS and Raman spectroscopy aims to study the chemistry and mineralogy of the Martian regolith. However, unlike the previously mentioned IR spectrometer, the SuperCam one is a passive visible and near IR spectrometer (VISIR), which is known as VIS-NIR-SWIR reflectance spectrometer. Passive VISIR spectroscopy is widely used for the detection and identification of both organic and inorganic compounds. This passive technique does not have any problem with the measurement distance, since they can observe up to the horizon because sunlight is absorbed by molecules so there is no need of any excitation source. The reflectance spectra are characteristic of the molecules composing the target as they absorb at frequencies driven by their vibrational frequencies.

Considering all this, the SuperCam VISIR will be used to identify remotely minerals at the mm-scale from the vicinity of the rover to distant outcrops. It is located on the bottom of the mast unit together with other SuperCam instruments, such as the RMI, the telescope and the 1064 and 532 nm lasers, among others. The passive VISIR use an acousto-optic tunable filter (AOTF) exited by a RF signal to diffract 256 different wavelengths ranging between 1300 and 2600 nm on two photodiodes to produce a single spectrum in about 80 s. The spectral resolution spans from 5 to 20 nm and it has a FWHM of 30 cm^{-1}. Its performance temperature range goes from −35 to −5 °C [149,164,165].

Among the three IR spectrometers described so far, the SuperCam spectrometer is the one with the worst spectral resolution. However, it should be noted that SuperCam is the first instrument of all those described that combines three different spectroscopies simultaneously to measure the same point. Moreover, working remotely will obviously have less accurate results than *in situ* measurements done inside the instruments themselves with sample collection. Although it has less spectral resolution than the other IR spectrometers, the combination of the IR results with the Raman and the LIBS ones will make great advances in the knowledge of the Martian surface mineralogy.

As has been explained above, MarSCoDe will have a LIBS spectrometer analyzing the laser-excited plasma from the UV to the NIR. Besides, MarSCoDe will be also equipped with a passive spectrometer operating from the NIR to the short-wave infrared (SWIR). The MarSCoDe will be a spectral detection instrument with a combination of active-passive detection techniques. Therefore, by combining the 240–850 nm spectral range of the LIBS module and the 850–2400 nm spectral range of the IR module, it will acquire the passive mode covering 240–2400 nm [106,166].

The main function of the SWIR will be collecting the reflected solar radiation by the Martian surface and transmit it to the SWIR spectrometer. Its spectral resolution will be between 3 and 12 nm. Like SuperCam's VISIR spectrometer, the SWIR will use an AOTF crystal as the dispersive component and for band selection. The total mass of the MarSCoDe instrument will be 16.4 Kg and it will have a power consumption of 64 W. MarSCoDe will work while the rover will be in a stationary mode [106,166].

The following rover to incorporate IR spectrometers in its scientific payload will be the Rosalind Franklin rover. This rover will be equipped with three different IR instruments: the Infrared Spectrometer for ExoMars (ISEM), the Mars Multispectral Imager for Subsurface Studies (Ma-MISS) and MicrOmega.

ISEM will assess the mineralogical composition of surface targets. Working together with PanCam, ISEM will contribute to the selection of suitable samples for further analysis by other instruments. ISEM will be a pencil-beam infrared spectrometer that will measure reflected solar radiation in the near infrared range for context assessment of the surface mineralogy in the vicinity of the ExoMars rover. The instrument will be located in the mast of the rover and will cover the spectral range from 3.3 nm at 1.15 μm to 28 nm at 3.30 μm with a spectral resolution of ∼ 25 cm^{-1}. The spectrometer will also use a AOTF and the total mass of the instrument will be 1.74 Kg [167].

Ma-MISS will be located inside the drill and it will be the instrument in closest contact with the Martian surface. The Martian surface is highly influenced by external processes such as weathering, erosion, sedimentation and impact, which alter its original properties. In this way, Ma-MISS's main science objective is to study the Martian subsurface to analyze partially unaltered material. This instrument will image the walls of the borehole created by the drill to study the Martian mineralogy and rock formation. As the rover drills into the upper surface of Mars, Ma-MISS will illuminate the hole's cylindrical wall through a transparent window situated in the drill tool. It will capture the reflected light and analyze its spectrum. This instrument will exploit the movement of the drill to acquire data form all around the borehole. The rotation of the instrument as it descends will allow images to be built up in both horizontal (ring image) and vertical sequences (column image). This will provide valuable information for the study of subsurface soil and rock layers, the distribution and state of water-related minerals and it will help to characterize the geophysical Martian environment [168,169].

The spectrometer will perform IR spectral reflectance investigations in the 400–2200 nm range to characterize the mineralogy at depths between 0 and 2 m. Besides, it will provide high precision data with 20 nm of spectral resolution [168,169].

Finally, MicrOmega will be a micro-imaging system designed to identify, at grain scale, the mineralogical and the molecular composition of the Martian samples collected by the ExoMars drill. This instrument will be included in the suite of the analytical

Table 1
Features of each of the IR spectrometers that aim to analyze *in situ* the Martian surface.

Instrument	Rover	Analysis site	Type of sample	Type of analysis	Target	Spectral range/nm	Spectral resolution
Mini-TES	Spirit and Opportunity	Inside the rover	Surface	Imaging	Minerals	5000–29000	10 cm^{-1}
TLS	Curiosity	Inside the rover	Surface	Punctual	Specific organic molecules	2780 and 3270	0.0005 cm^{-1}
SuperCam	Perseverance	Remotely	Surface	Punctual	Minerals	1300–2600	30 cm^{-1}
MarSCoDe	Tianwen-1	Remotely	Surface	Punctual	Minerals	850–2400	3–12 nm
ISEM	Rosalind Franklin	Remotely	Surface	Punctual	Minerals	3.3–28	25 cm^{-1}
Ma-MISS	Rosalind Franklin	Inside the rover	Subsurface	Imaging	Minerals	400–2200	20 nm
MicrOmega	Rosalind Franklin	Inside the rover	Surface	Punctual and imaging	Minerals	500–3650	20-30 cm^{-1}

Table 2
Pros and cons of using *in situ* analytical techniques to measure the geochemistry of non-terrestrial samples.

In situ analytical techniques	
PROS	CONS
✓Latest technology. ✓Downsizing. ✓Automation and monitorization. ✓Samples do not undergone any change in molecular/mineral structure or chemistry as pretreatment is avoided. ✓Same environmental measurement conditions as samples.	× Worse detection limits. × Slower but reliable instrument-Earth connections. × More expensive. × High risk of being damaged. × Limitation of the analysis due to environmental conditions and energy constrains.

laboratory together with MOMA and the RLS. All of them will characterize the collected samples and specifically the organic substances they may contain. MicrOmega will consist of a visible light microscope and a near infrared imaging spectrometer. The total mass of the instrument will be less than 2.4 Kg and its dimensions will be 17 × 16 × 11 cm. The instrument will use an AOTF and its associated detector with a high spectral sampling of 2–14 nm. It will acquire high resolution monochromatic images in a spectral range that will go from 500 to 3650 nm [170].

Each of the Rosalind Franklin rover instruments will have a different function, so it is difficult to compare them with each other. Even more difficult is to compare the seven instruments that use IR spectroscopy as they were built following different needs and for very different aims. Some perform infrared imaging, others small-scale spot analysis, others carry out it remotely at bigger scale, etc. Table 1 summarizes some features that allow differentiating between the seven instruments described.

4. Discussion: pros and cons of using *in situ* and laboratory analytical techniques to study Martian geochemistry

Meteorites are the only samples available on Earth coming from Mars. These samples can be analyzed by laboratory analytical techniques and provide very relevant information, such as mineralogy and petrology.

Table 3
Pros and cons of using laboratory analytical techniques to measure the geochemistry of non-terrestrial samples.

Laboratory analytical techniques	
PROS	CONS
✓Better detection limits. ✓Faster instrument-Earth connections. ✓Cheaper. ✓Downsizing. ✓Some, but not all, are automatic. ✓Low risk of being damaged. ✓Imaging possibility	× Samples could undergone some changes in molecular structure or chemistry. × Different environmental measurement conditions than those of the samples.

All Martian meteorites have suffered mineral transformations due to the high pressure and/or temperature changes during their travel from the Martian surface to the Earth crossing the Earth atmosphere. Because of this, meteorites are considered altered samples and are not fully representative of the celestial body they belong to. In this way, it is possible to know the primary and secondary mineral phases and those of alteration or weathering. These weathering products may hinder the interpretation of the original mineral phases (primary and secondary). Despite this complexity, it is feasible to recreate the history of the geochemical evolution of the Martian surface.

This problem will be solved when the first samples return form Mars. Those samples will be analyzed with the widest analytical techniques available in the specialized laboratories that study extraterrestrial materials. However, this will occur in the early 2030s. Until those dates, Martian meteorites will be the only samples from Mars available on Earth to be studied with laboratory analytical techniques.

In situ analyses on the Martian surface with the instruments on board the different missions are the only alternative to study Martian materials that have not been subjected to geochemical alteration events.

The number of instruments on board the different missions has increased continuously over time. In fact, the current methodologies used in laboratories for the geochemical characterization of meteorites have been included as part of the instrument payload of Martian rovers and/or landers. In order to get the analytical techniques on board the spacecraft, several requirements were satisfied: size was minimized, power consumption reduced, sensitivity and accuracy improved, portability enhanced, mechanical and shock resistance improved, reliability under space conditions, and more.

Therefore, reaching the requirements of space exploration has been, is and will be a great challenge for the development of analytical chemistry.

For example, as indicated in the historical background section, the first analytical instrument that went to space for the purpose of studying the geochemistry of a non-terrestrial body was XRF implemented in the Viking landers. Then the first APXS was introduced in the Sojourner rover, substantially miniaturized and improved with regard to the XRF instrument.

Thanks to the miniaturization, the APXS could be mounted later on robotic arms, providing the possibility to move the instrument to the target of measurement, like the MER missions demonstrated. Then the first LIBS instrument was developed for remote analysis of targets in the Curiosity rover, having even less weight but increasing the analytical capabilities as the number of analyzed rocks/soils/veins increased by more than ten times per working days. And now, the Perseverance rover implements, together with LIBS, the first XRF imaging spectrometer (PIXL) to improve the characterization of the chemical elements in the samples under analyses.

This example clearly shows the achieved improvements not only in the analytical capabilities of instruments to perform the best chemical analysis on the Martian surface but also the most quick ones. The Perseverance rover that implements the remote LIBS analyzer and the proximity XRF image analyzer will allow to obtain more than a hundred elemental measurements and a couple of XRF images per working day.

Since the MER mission that equiped the Opportunity and Spirit rovers with the Athena Science Payload, composed of six instruments and a Rock Abrasion Tool working on the same sample [44], the collaborative science has been possible on Mars, when a similar instrument is not available on Earth. Here we use several instruments to analyze the same sample that is moved from one instrument to the next. However, at micrometric scale it is quite difficult to perform laboratory analyses from several techniques exactly on the same spot. But this capability was achieved in the MER mission, later in the MSL mission [50] and nowadays in the Mars2020 through the complex SuperCam instrument [105], composed by remote and proximity high resolution cameras, the LIBS analyzer for detection of chemical elements, the VISIR analyser for minerals and organic molecules sensitive to the visible-NIR radiation, the Raman analyzer and the Luminiscence analyzer.

Therefore the advances in analytical instrumentation made in response to the needs of space exploration are not only applicable to *in situ* analysis techniques. As costs have been reduced, these innovative improvements could have been spread to laboratory instrumentation. However, until today very few laboratory analytical instruments can do collaborative science using a single benchtop. This means that only one laboratory instrument can make measurements with at least 3–4 different analytical techniques on the same microscopic spot, like the SEM/EDS-Raman instrument, which is commonly used to characterize meteorites [4].

This is the case of the SuperCam instrument onboard the Perseverance rover, which is the most modern analytical instrument used by space exploration. However, it is expected that in few years the concept of collaborative science will be extended to laboratory setups, coupling several analytical techniques in the same benchtop instrument. Even, such improvements will be implemented in the near future in portable instrument for fields analyses.

In the near future, one of the best instrumental suites for combined science will be inside the ALD on board the Exomars 2022 rover. Its carousel will be able to place a small amount of sample under the common observation of the MicrOmega, RLS and MOMA instruments.

Table 2 and Table 3 show the pros and cons of both alternatives to analyze/characterize mineral samples (outcrops, isolated rocks, weathering patinas, indurated soils, fine-grained soils and dust) like those checked on Mars. Moreover, the quantitative data coming from Mars are of very good quality since daily calibrations can be performed to check the trueness of the results and uncertainty values are always given with the mean values for concentrations. And this is made at micrometric scale (spots of less than 300 μm) enhancing the capability to focus on single mineral grains, obtaining the highest mineral diversity of Martian rocks, similar to the Earth ones where more than 5–8 minerals can be present at high, low and trace levels.

5. Conclusions: the advance of the analytical science with Mars exploration

The development of the scientific instruments for the different *in situ* Mars exploration missions, using landers and/or rovers, must be considered as one of the most important human effort to improve the Analytical Science. Table 4 summarizes the analytical instruments included in the successful missions landing on Mars. In the first column of Table 4 the number of scientific contributions, accessed through Scopus site are indicated for each mission, showing that more than 5700 research papers have been published in the 45 last years about *in situ* Mars exploration.

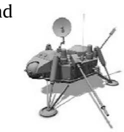
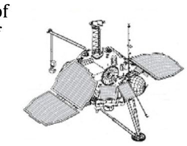
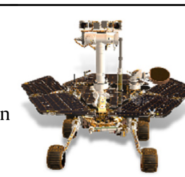
It is interesting to observe how the complexity of the analytical instruments included in the payload of the landers and rovers has increased with years, as observed in the 5th column of Table 4. This increase was mainly due to two reasons. On the one hand, the missions were designed based on the achievements of the previous ones, so their complexity increased. On the other hand, the capabilities of the industry to produce components with the high technical constrains for analytical instrumentation in adverse conditions increased with time. The consequence is the increasing number of research contributions from the first missions until nowadays because the scientific community had access to a great amount of data, being more and more complex as the different instruments implemented in the payloads were contributing significantly.

Moreover, the access to public repositories where data from the different missions are available to the entire scientific community, has increased the number of contributions from teams not included initially in the Science Teams of the missions. In this sense, the initial and revised data obtained by the two Viking landers must be highlighted, as the number of papers is higher than with more recent missions. Some people did not believe on the results obtained by the Viking landers, in particular those related to the presence of organic compounds on Mars. Fortunately, the results of the SAM instrument onboard the Curiosity rover were coincident and validated the GCMS results from the Viking landers, showing the great diversity of organic molecules (persistent and volatiles) on Mars.

The research contributions of the MGS and Mars Express must also be highlighted although these are mainly coming from the remote visible and infrared observations because the two landers failed. Up to today, the most exciting mission has been MSL with more than 1000 contributions in the ten years of the mission, but if we look at the papers coming from the Mars 2020 mission (just landed in February 2021) and Exomars mission (not launched until September 2022), we can expect that these two missions will be even more productive from the science point of view because the papers published until now are related to the science developed in preparation of the mission and optimization of the different payload instruments. This fact is also due, without any doubt, to the increase in the number of analytical instruments included in both Perseverance and Rosalind Franklin rovers, instruments that are going to work in a combined form, enhancing the finding capabilities due to the synergies among them.

When the data from Perseverance and Rosalind Franklin are available in the NASA and ESA repositories, the scientific community will have the chance to study and use such experimental information that will not be 100% used by the science teams of both missions, due to the enormous amount of data that will come in the

Table 4
Summary of the robotic missions to Mars that have investigated, are investigating and will investigate *in situ* the Martian surface using different analytical techniques. The number between parentheses in the Mission column indicates the scientific papers summarized in Scopus.

Mission	Craft name	Launch, landing and last communication date	Landing site	Analytical Instruments	Important data	Image of the spacecraft
Viking Project (591)	Viking 1 Lander	1975/07/20 1976/07/20 1982/11/11	Chryse Planitia	XRF Biology Laboratory GC/MS	• First GC/MS instrument, XRF spectrometer and biology lab on Mars • Classification of SNS meteorites	
	Viking 2 Lander	1975/09/09 1976/09/03 1980/04/11	Utopia Planitia			
Mars Pathfinder Project (438)	Sojourner Rover	1996/12/04 1997/07/04 1997/10/07	Ares Vallis (Chryse Planitia)	APXS	• First APXS instrument on Martian surface • Simplest and cheapest mission to bring a spacecraft to the surface of Mars	
	Carl Sagan Memorial Station Lander			IMP	• The rover communicated with Earth through the lander	
Mars Surveyor (430)	Mars Polar Lander	1999/01/03 1999/12/03 1999/12/03	Planum Australe (north pole)	Lander Failed Thermal evolved gas analyzer LIDAR	• Interest in studying the only known examples of extraterrestrial ice-sheets comparable to those of the Earth	
Mars Express (638)	Beagle-2 Lander	2003/06/02 2003/12/25 2003/12/25	Isidis Planitia	Lander Failed GAP MIMOS XRF	• First lander of ESA on Mars • First lander aiming to study the mineralogy of Mars with MIMOS	
Mars Exploration Rovers (MER) (437)	MER-A (Spirit Rover)	2003/06/10 2004/01/04 2010/03/22	Gusev Crater (Aeolis Quadrangle)	PanCam Mini-TES Mösbauer APXS RAT	• Detection of pure silica (MER-A) • Detection of sulfate rock coverings (MER-A) • Detection of hematite-blueberries (MER-B) • Discovery of jarosite (MER-B) • Some of the minerals detected are formed in presence of water.	
Mars Exploration Rovers (MER) (810)	MER-B (Opportunity Rover)	2003/07/07 2004/01/24 2018/03/10	Eagle Crater (Meridiani Planum)			
Phoenix Mars Mission (312)	Phoenix Mars Lander	2007/08/04 2008/06/25 2008/11/02	Green Valley (Vastias Borealis)	WCL MECA TEGA	• Detection of perchlorates, chlorides, sulfates and carbonates	
Mars Science Laboratory (MSL) (1023)	Curiosity Rover	2011/11/26 2012/08/05 Still operating	Gale Crater (Elysium Planitia)	APXS MAHLI ChemCam CheMin SAM MastCam	• First LIBS and XRD instruments on Mars • First time an instrument is equiped with more than one analytical technique (SAM) • Longer-lasting mission (still operating) and with greater geochemical results	

(*continued on next page*)

Table 4 (*continued*)

Mission	Craft name	Launch, landing and last communication date	Landing site	Analytical Instruments	Important data	Image of the spacecraft
InSight Mission (601)	InSight Lander	2018/05/05 2018/11/26 Still operating	Elysium Planitia	SEIS HP^3 RISE APSS	• This mission did not study the geochemistry of Mars • Discovery that there was a time when the surfaces of Mars and Earth were similar	
Mars2020 (556)	Perseve-rance Rover	2020/07/30 2021/02/18 –	Jezero Crater (Isidis Planitia)	PIXL SHERLOC WATSON SuperCam RIMFAX MastcamZ	• The rover will collect samples to return to Earth throughout MSR mission • First time to employ remote analytical techniques, such as SuperCam, among others • First time to bring a Raman spectrometer to Mars aiming to study the mineralogy	
Tianwen-1 Mission (10)	Tianwen-1 Rover	2020/07/23 2021/05/14 –	Utopia Planitia	MarsCoDe MSCam NaTeCam RoPeR RoMAG MCS	• China's first Mars exploration mission	
ExoMars (706)	Rosalind Franklin Rover	– – –	Oxia Planum	PanCam ISEM, CLUPI WISDOM ADRON-RM Ma-MISS MOMA RLS MicrOmega	• First mission to combine the capability to move and to study Mars at variable depths • First the geological context will be analyzed and then micro-analyses will be performed • First Sample Preparation and Distribution System	
MMX Mission (43)	MMX Rover	– – –	Phobos	RAX miniRAD	• First JAXA mission to study Mars and its moons • First rover to reach Phobos	

near future. Thus, we can imaging a large number of contributions at the end of this decade.

The complexity of instruments make necessary the implementation of calibrations targets. The first calibration target in the sense of an analytical calibration tool to guaranty the trueness of the quantitative results of elements present in the samples was implemented in the ChemCam instrument onboard Curiosity [104]. The next generation of calibration targets was incorporated in Perseverance to assess the quality of the calibration of the five spectrometers in the SuperCam instrument and also to check periodically the trueness of the elemental quantitative values obtained with LIBS. Together with the calibration target, SuperCam also incorporates internal checks to evaluate reproducibility [105], being the most complex analytical instrument ever manufactured.

The instruments included in Perseverance are not available nowadays for Earth applications. This has been a constant in the development of new analytical devices for Space Exploration that, within years, have been transformed in adapted instruments for Earth applications. And this will happen again with the different instruments installed in Perseverance and Rosalind Franklin rovers. It is only a matter of few years.

Another characteristic of the development of analytical instruments for *in situ* exploration on Mars has been miniaturization. This is a consequence of the limited weight for the payload instruments. The different teams involved in the construction of the instrument systems and subsystems have afforded the necessity to reduce size and weight but maintaining a high performance in the devices. For example, the laser for the Raman instrument in Exomars has reduce its size until $5 \times 3 \times 1$ cm and this development will come in few years for the new generation of Raman instruments for Earth applications.

The next generation of space instruments will consider the development of new detectors, with imaging capabilities (not only a spot but a whole 2D matrix), something that has been developed for the PIXL instrument in Perseverance, but at microscopic level. In this sense, the clean laboratory known as ADL (Analytical Drawer Laboratory) in Rosalind Franklin, with spectroscopic devices for microscopic analysis and mass spectrometry with and without previous GC, is showing the way for future developments.

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Author contributions

The four authors have compiled the references and analyzed the bibliography. J. Huidobro wrote the initial draft and compiled figures. J. Aramendia, G. Arana and J.M. Madariaga revised the draft to the final version.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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