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Exobiology

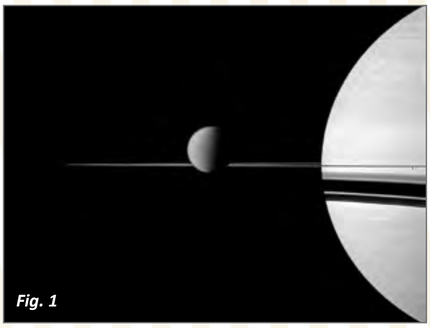

Fig. 1

Fig. 2

Fig. 3

In France, scientific teams of astrobiologists have been supported by grants from the French space agency (CNES) for experiments in space, operation or preparation of missions to explore target bodies for Astrobiology or to prepare relevant future space missions.

Planetary missions

The joint American and Italian CASSINI mission, extended up to 2017, is still inspiring work on the chemical reactions in the atmosphere of Titan based either on observations or laboratory work [1]. The molecular characterization of tholins is a continuous challenge. NMR or MALDI-TOF analysis of tholins gave new insight on those products as well as the effect of hydrolysis mimicking possible conditions they could encounter on Titan. Finally the synchrotron UV light is a powerful mean to simulate the atmospheric chemical reaction occurring in the outer layer of the atmosphere of Titan [2].

After a significant reshuffling based on a new partnership with Russia, the *Exomars* program from ESA is on track for the launch of its two missions, in 2016 and 2018 respectively. Contributions to the Russian payload of the Trace Gas Orbiter are finalized as well as contributions to a DLR led technical experiment to be implemented on the Entry descent and landing Demonstration Module (EDM). The French teams involved in the instruments for the Pasteur payload of the rover to be launched in 2018, are now producing prototypes tested during field campaigns and models to be delivered to the European Space Agency. The teams are very collaborative and this translates into papers underlining the cooperation spirit and preparing future operations [3].

The International Space Analogue Rockstore (ISAR) developed in Orléans [4] is now available for testing and calibrating the instruments to be flown on space missions. In order to prepare the EXOMARS mission and the teamwork which will be required, several samples from ISAR were proposed for a "blind test" of the EXOMARS 2018 mission instruments.

Experiments in low Earth orbit

The analysis of the EXPOSE-R samples which were retrieved in 2011 are almost analyzed. The samples were distributed few weeks later. Most of the results are already published and few papers are still pending. Science results combined with laboratory experiments give new insight of interplanetary chemistry [5]. Scientific teams are completing the preparation of the next experiments selected in 2009. EXPOSE R2 is now slated for launch to the ISS, by ESA, during the second half of 2014. EXPOSE R2 will not be a carbon copy of the first experiment. New mixture of gas, new products will be exposed. Some samples will be dedicated to a simulation of the exposure of Martian soil to the Sun light filtered by the Martian atmosphere. Finally the sensitivity to the space environment of molecules to be used in Biochips will be evaluated in this experiment [6].

From space to the laboratory and vice versa

Several teams are working on the relationships between cosmochemistry and the origin of life. They are irradiating various type of ices maintained at very low temperatures (50 to 90 K). After the work reported in the former edition [7], the analysis of various organic compounds by a range of analytical instruments, including the very high resolution mass spectrometer was performed [8]. The molecular richness that was highlighted can be considered as the "first step" of the complex abiotic organic matter in extraterrestrial media. This initial matter, that may be rather universal, could then evolve toward more processed materials in parent bodies, such as comets and asteroids, materials that are then observed and subsequently analyzed in meteorites found on Earth.

Similar instruments, and particularly the high resolution mass spectrometer, were used to decipher the complexity of the tholins produced in various conditions [9].

While the instrument ICAPS dedicated to the study of the optical properties of dust particles in space is still in development at ESA for a flight on board the International Space Station, French

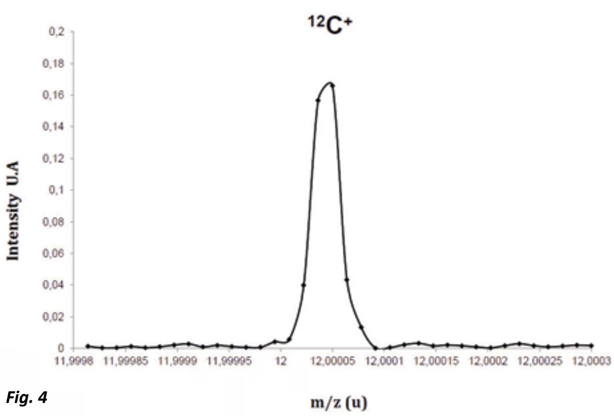

Fig. 4

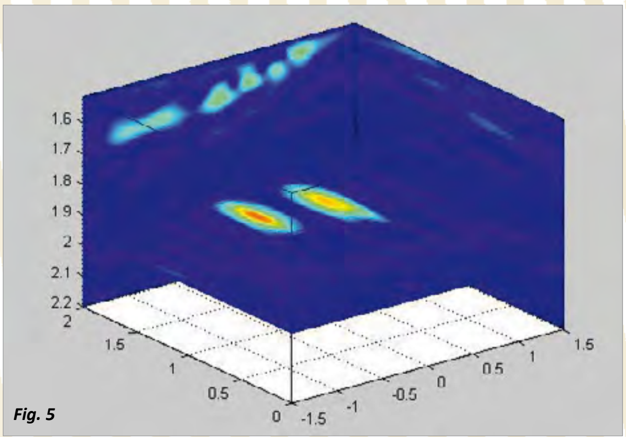

Fig. 5

teams are using the parabolic flights and the PROGRA2 facility to study the light scattering properties of tholins, analogues of cometary particles or other aggregates [10].

New instruments

Most of the activities developed under the research and development activities aim to the design of new instruments fitting with the constraints of space exploration. The achievement of the work of a container dedicated to the study under stringent containment of possible future Martian samples is now evolving toward automation for 3D scanning.

The interest of the Electron Paramagnetic Resonance (EPR) was validated [11] and the teams are now working on the adaptation of the instrument to space conditions. The reduction in mass along with a simplification of the instrument open the way for a first prototype.

The Scientific Prospective Seminar held in La Rochelle which gathered the science community to give directions for the next five years of research in space, outlined the necessity to pursue the effort in developing new instruments (like EPR) or high resolution mass spectroscopy devices based on Orbitrap.

Outreach

The agency supported, an annual astrobiology course organized by Dr Muriel Gargaud, University Paris XII and the University of Bordeaux, dedicated to PhD students (RED, Rencontres d'Exobiologie pour Doctorants).
Finally with the support of the agency as well as several other institutions in Europe and Canada, the scientific community is working hard on the preparation of the second edition of the "Encyclopedia of Astrobiology" [12].

[Fig. 1]
The Cassini spacecraft views Saturn with a selection of its moons in varying sizes (center: Titan, far right and smaller: Encelade).
© NASA/JPL/Space Science Institute

[Fig. 2]
PROGRA2
© Bertrand Gaubicher

[Fig. 3]
ESA testing of instruments for EXOMARS: Wisdom antenna on the forefront of the Bridget Rover during the SFAER experiment in Chile.
© V. Ciarletti/LATMOS

[Fig. 4]
Focus on the Carbon 12 of an adenine sample's mass spectrum, using the proto flight model Orbitrap cell (LPC2E). Mass resolution at mid-height: 363 000.
© Consortium ORBITRAP

[Fig. 5]
ESA testing of instruments for EXOMARS: 3D representation of the subsurface from WISDOM data. Two scaterrers buried two meters below the surface are localized. 2013 POLARES experiment, Dachstein, Austria.
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Exobiology

Titan's tholins and internal ocean models

Tholins de Titan et modèles de l'océan interne

➔ **Abstract:** The possible evolution of organic aerosols on Titan surface with the cryomagma coming from the internal ocean has been mimicked using Titan's tholins. They were placed in water-ammonia solutions containing carbonate and/or sulfide. The resulting products were analyzed using chemical derivatization-GC-MS analysis. They include urea, amino acids and carboxylic acids. Carbonates inhibit the formation of some amino acids, but favor that of glycerol, homoserine and 2-butenoic acid.

➔ **Résumé :** L'évolution possible des aérosols organiques à la surface de Titan avec le cryomagma venant de l'océan interne a été simulée à l'aide de tholins, mis dans l'eau ammoniaquée contenant des carbonates et/ou des sulfures. Les produits obtenus ont été analysés par dérivatisation chimique-CPG-SM. Ils incluent urée, acides aminés et acides carboxyliques. Les carbonates inhibent la formation de certains acides aminés mais favorisent celle du glycérol, de l'homosérine et de l'acide 2-butenoïque.

Titan, the largest satellite of Saturn looks like an evolving planet, geologically active, with a complex organic chemistry occurring in the ionosphere where high molecular weight ions are present [1]. These are likely to be involved in the formation of aerosols analyzed in the lower atmosphere. CASSINI-HUYGENS has demonstrated that the chemical composition of Titan's aerosols is similar to that of laboratory Titan's tholins. Many laboratory works have been carried out on Titan tholins [2]. The plasma tholins produced at LISA can release large amounts of HCN and NH_3 when pyrolyzed at 600 °C, similarly to Titan's aerosols. These plasma tholins can thus be considered as good laboratory analogues of Titan's aerosols and can be used to study in Earth laboratory the properties of Titan's atmospheric particles.

CASSINI-HUYGENS data have revealed a highly diversified solid surface on Titan with features that suggest possible cryovolcanic structures. Moreover, the existence of an internal liquid water ocean, containing a few percent of ammonia has been proposed. This model of Titan's interior has recently been supported by CASSINI-HUYGENS observations. It has also been proposed that ammonia-water mixtures can erupt from the putative subsurface ocean leading to cryovolcanism. From recent works on the internal ocean formation [3] we have estimated a possible composition of the internal ocean. The results are summarized in Fig. 1. The main minor constituents are carbonates, with a concentration close to 0.1 mole/l, and hydrogenosulfide with a concentration of about 0.24 mole/l. Titan's aerosols, once on the surface, may chemically evolve in spite of the low surface temperature (94-92 K) if they are in contact with the cryomagma of composition similar to the internal ocean. Big impacts on Titan's surface may episodically melt the ice crust and form liquid water oases that could stay in the liquid state for up to several thousands of years. This could favor a chemical evolution of the organic components of atmospheric aerosols that settled down to the surface. Otherwise, these organics may also evolve at much slower chemical rates in the absence of violent-impact episodes.

Several experimental works have already been performed to study the low temperature hydrolysis of the macromolecular organics of the aerosols. The high temperature acidic hydrolysis of plasma-generated tholins produces a large variety of amino acids and other organics. The production of amino acids is still observed, when hydrolysis is performed with liquid water at neutral pH. Similar results are obtained from alkaline solutions, using water-ammonia mixtures. Now, what could be the influence of the presence of other species in the water mixture, such as carbonates and sulfides, likely to be present in the cryomagma at noticeable concentration? To answer that question we synthesized laboratory analogues of Titan's aerosols from a N_2:CH_4 (98:2) gas mixture irradiated in a low-temperature continuous-flow regime by a DC cold plasma discharge. We used a new system, avoiding any atmosphere contamination of the tholins during their recovery. The analogues were recovered, partitioned in several 10.0 mg samples and placed in different aqueous ammonia solutions at low temperature for 10 weeks [1]. One experiment was done without additional salt (Hydrolysis #1), one with 0,236 mol/l hydrogenosulfide (Hydrolysis #2), one was done with 0,092 mol/l carbonate (Hydrolysis #3), and one with 0,092 mol/l carbonate and 0,236 mol/l hydrogenosulfide (Hydrolysis #4). After 10 weeks of evolution, a chemical derivatization process was performed on the refractory phase of the aerosol analogues, with MTBSTFA in DMF. In the case of the hydrolyses done in the presence of salts, (Hydrolyses #2, #3 and #4) a preliminary extraction step using cation

Species	NH_3	NH_4^+	H^+	HO^-	CO_2(aq)	HCO_3^-	CO_3^{2-}	H_2S	HS^-	S^{2-}	Na^+
C (mol/L)	**2,88**	$6,8.10^{-3}$	$1,5.10^{-12}$	$6,8.10^{-3}$	$3,6.10^{-6}$	$2,72.10^{-3}$	**0,092**	$3,5.10^{-6}$	**0,236**	0,020	0,463

Fig. 1

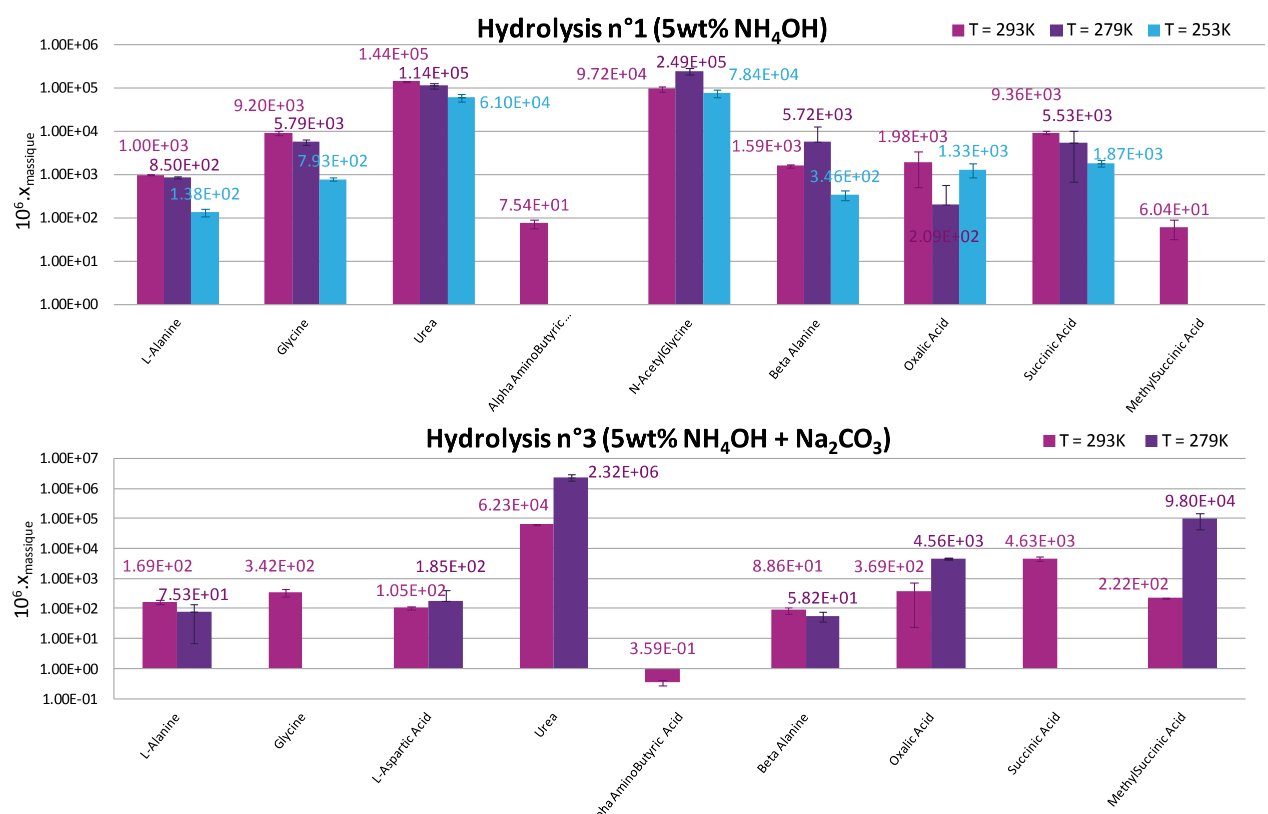

Fig. 2

exchange resin was done to remove the salts, the presence of which is not compatible with the derivatization. The hydrolysis products were then identified and semi-quantified by gas chromatography coupled to mass spectrometry.

Results related to Hydrolyses #1 and #3 are presented here. The results show (Fig. 2) that tholins are very reactive toward an oxygen source. Urea is among the main products of Titan's tholins hydrolysis in both cases. Several other organic compounds are produced. In Hydrolysis #1, they include amino acids: alanine, glycine, α-aminobutyric acid, Υ-aminobutyric acid, N-acetylglycine, β-alanine, oxalic acid, succinic acid and methylsuccinic acid. The presence of carbonate (Hydrolysis #3) inhibits the formation of several amino acids, particularly of Υ-aminobutyric acid, glycine and its derivatives. On the contrary, it induces the formation of aspartic acids, as well as of homoserine, glycerol and 2-butenoic acid.

Study of the potential role of sulfide (Hydrolyses #2 and #4) are currently in progress.

[Fig. 1]
Review of the possible anion composition of the likely sub-surface ocean. © Adapted from [3]

[Fig. 2]
Yields of formation of organic products obtained from Hydrolysis #1 (ammonia-water without salts) and Hydrolisis #3 (ammonia-water with carbonate). The yields are multiplied by 106 in order to fit with the logarithmic scale. © LISA/C. Brassé

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Exobiology

Calibration and testing of payload instrumentation for in situ space missions

Calibration et test de charges utiles pour des missions spatiales *in situ*

➔ **Abstract:** Success of *in situ* space missions depends largely on the ability of payload instruments to use complementary information provided by the different instruments in order to correctly identify rocks and minerals on the target surface. Normally each instrument is calibrated and tested individually. However, *in situ* rock and mineral identification requires testing the whole payload with real analogue materials in order for the results of each instrument to be understood.

➔ **Résumé :** Le succès des missions spatiales *in situ* dépend largement de la complémentarité des informations fournies par les instruments de la charge utile pour l'identification correcte des roches et des minéraux analysés. Cependant, les instruments sont généralement calibrés et testés séparément. Afin d'améliorer le niveau d'expertise des missions *in situ*, il apparaît donc pertinent de compléter ces phases préparatoires par une calibration globale des instruments d'une même charge utile utilisant des échantillons analogues de l'astre visité.

The results of recent *in situ* missions on Mars, the Mars Exploration Rovers and the Mars Science Laboratory, have underlined the difficulties of integrating information from different instruments to correctly identify rock types on Mars. Rocks consisting of the same elements may have very different mineralogy and origins. Bulk analyses of a rock will provide the general mineralogy but specifically located analyses will help understanding alteration or late-stage features, for instance associated with fractures. Improvement of *in situ* performance in terms of time and accuracy can be obtained by testing the entire payload suite with the same test materials.

The next mission to be launched to Mars will be the EXOMARS rover mission (ESA/ROSCOSMOS) in 2018. The main science objective of the mission is the search for traces of life but in order to achieve this, it is necessary to correctly determine the geological context of any potential biosignatures, emphasis being on organic molecules as biosignatures. The Pasteur payload includes a variety of cameras (panoramic, PanCam, high resolution, HR) and a CLose UP Imager (CLUPI). Mineral identification of rock outcrops will be made with a laser IR spectrometer (ISEM) located on the mast. The drill hole will be made by the infrared spectrometer (Ma_MISS). EXOMARS will have a drill that can penetrate up to 2 m below the surface to reach rocks that have been protected from radiation and oxidation processes operating at the surface of Mars. The crushed drill core will be made by a visible-IR imager and spectrometer (MicrOmega). The Raman spectrometer (RLS) and MOMA, a GC-MS and LD-MS will be used to identify organic molecules. IR analyses will be made on distant rock.

We used two Mars-analogue samples from the International Space Analogue Rockstore (ISAR, www.isar.cnrs-orleans.fr [1]) to perform a blind test using prototypes of the EXOMARS rover instruments related to the geological context (close-up imager, IR and Raman spectrometers) [2]. Samples were a volcanic rock (komatiite, Fig. 1) with a composition particularly close to that of Martian basalt, i.e. rich in elements Mg and Fe, and volcanic sand deposited in a shallow-water, aqueous environment (Fig. 2). Both rocks were formed on the early Earth at a period equivalent to the Late Noachian/Early Hesperion on Mars. They are therefore ideal analogues for the kinds of Martian terrains that will be the object of the EXOMARS mission. Moreover, the volcanic sands contain cryptic traces of fossil primitive life forms that are similar to what could be found on Mars [3-4]. This first test, however, concerned principally the geological identification of the rocks.

On the basis of a rock surface cut to imitate the surface of a drill hole, each instrument team provided an initial interpretation of the mineralogical composition of the rocks based on their own databases. These data were complemented with satellite images and photography of the relevant outcrops (representing orbital and panoramic camera data, as will be available during the EXOMARS mission) before being presented to a group of independent geologists tasked with interpreting the results. Our test results show that photography of the outcrops and close up imagery of the samples permitted identification of the rock type by trained geologists but their interpretation was confused by the preliminary mineral identifications provided by individual instrument teams. However, after cross-checking data between the different instruments and iteration of the identifications, it was possible for geologists to reach a reasoned interpretation of the rocks.

Thus, while rock type could be identified visually, correct interpretation of the processes affecting the rock after its formation could only be achieved using the spectroscopic data.

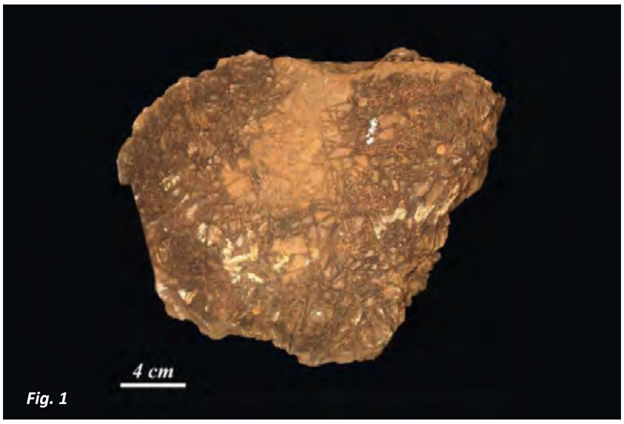

Fig. 1

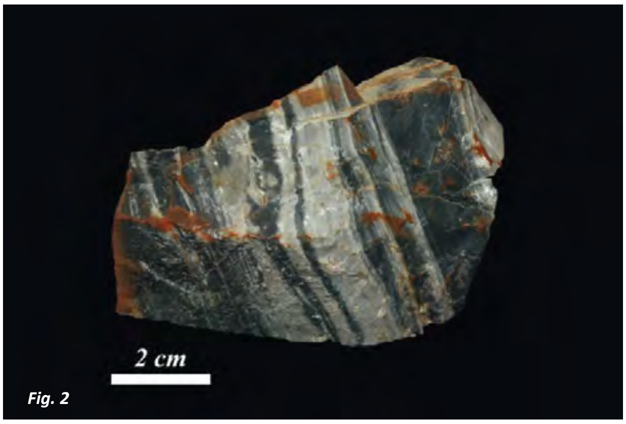

Fig. 2

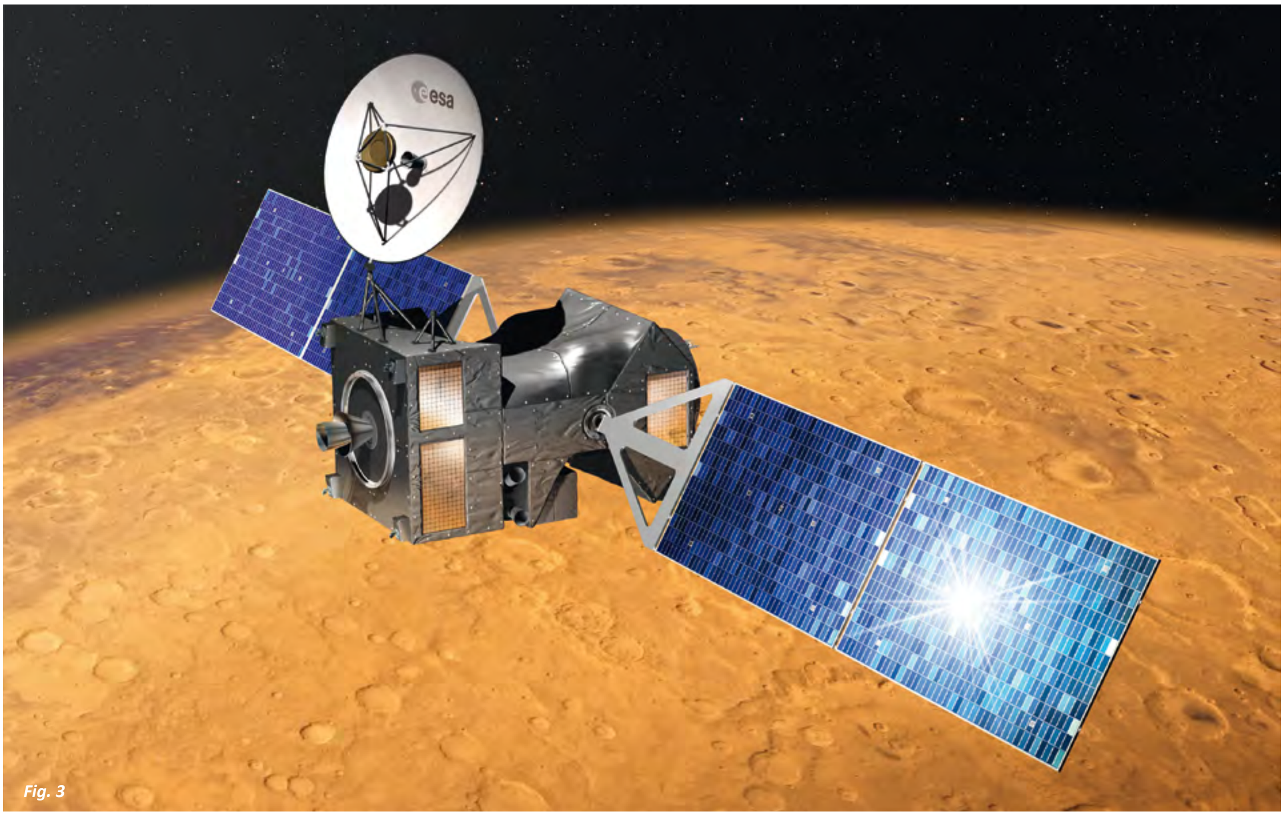

Fig. 3

In this case, both rocks had undergone alteration by water with consequent effects on the mineralogy. This interpretation is important because aqueous alteration is an extremely important feature in terms of signs of habitability.

This test underlines the necessity of cross-testing payload instruments using the same suite of analogue rocks (which are complicated compared to pure minerals) to optimize understanding of each instrument's performance and instrument's best complementary use. It also demonstrates the good complementarity of the EXOMARS instrument suite.

[Fig. 1]
Mars-analogue volcanic rock (komatiite) used for blind testing the EXOMARS context instruments. © ISAR

[Fig. 2]
Mars-analogue volcanic sand, deposited in an aqueous environment, used for blind testing the EXOMARS context instrumentation. © ISAR

[Fig. 3]
Artist view of the EXOMARS probe.
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