Planetary and Space Science 67 (2012) 1–13

Contents lists available at SciVerse ScienceDirect

Planetary and Space Science

journal homepage: www.elsevier.com/locate/pss

The influence of mineralogy on recovering organic acids from Mars analogue materials using the "one-pot" derivatization experiment on the Sample Analysis at Mars (SAM) instrument suite

F. Stalport [a,b,c,*], D.P. Glavin [c], J.L. Eigenbrode [c], D. Bish [d], D. Blake [e], P. Coll [a,b], C. Szopa [f,g,h,i,j], A. Buch [k], A. McAdam [c], J.P. Dworkin [c], P.R. Mahaffy [c]

[a] LISA, Univ. Paris Diderot, Sorbonne Paris Cité, UMR CNRS 7583, 61 Avenue du Général de Gaule, 94010 Créteil Cedex, France
[b] Univ. Paris Est Créteil, UMR CNRS 7583, 61 Avenue du Général de Gaule, 94010 Créteil Cedex, France
[c] NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA
[d] Indiana University, Bloomington, IN 47405, USA
[e] NASA Ames Research Center, Moffett Field, CA 94035, USA
[f] LATMOS-UPMC Univ. Paris 06, 4 place Jussieu, 75005 Paris Cedex, France
[g] Université Versailles St-Quentin, 4 place Jussieu, 75005 Paris Cedex, France
[h] CNRS/INSU, LATMOS-IPSL, 4 place Jussieu, 75005 Paris Cedex, France
[i] IPSL, France
[j] CNRS INSU, Quartier des Garennes, 11 Boulevard d'Alembert, 78280 Guyancourt, France
[k] LGPM Ecole Centrale Paris, Grande Voie des Vignes, 92295 Chatenay-Malabry Cedex, France

ARTICLE INFO

Article history:
Received 25 February 2011
Received in revised form
23 February 2012
Accepted 25 February 2012
Available online 7 March 2012

Keywords:
Mars
SAM
MSL
Derivatization
Organic matter

ABSTRACT

The search for complex organic molecules on Mars, including important biomolecules such as amino acids and carboxylic acids, will require a chemical extraction and a derivatization step to transform these organic compounds into species that are sufficiently volatile to be detected by gas chromatography mass spectrometry (GCMS). We have developed a "one-pot" extraction and chemical derivatization protocol using *N*-methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide (MTBSTFA) and dimethylformamide (DMF) for the Sample Analysis at Mars (SAM) experiment instrument suite on NASA's the Mars Science Laboratory (MSL) mission. The temperature and duration of the derivatization reaction, pre-concentration of chemical derivatives, and gas chromatographic separation parameters have been optimized under SAM instrument design constraints. MTBSTFA/DMF extraction and derivatization at 300 °C for several minutes of a variety of terrestrial Mars analog materials facilitated the detection of amino acids and carboxylic acids in a surface soil sample collected from the Atacama Desert and a carbonate-rich stromatolite sample from Svalbard. However, the rapid reaction of MTBSTFA with water in several analog materials that contained high abundances of hydrated minerals, and the possible deactivation of derivatized compounds by iron oxides, as detected by XRD/XRF using the CheMin field unit Terra, proved to be highly problematic for the direct extraction of organics using MTBSTFA. The combination of pyrolysis and two different wet-chemical derivatization methods employed by SAM should enable a wide range of organic compounds to be detected by GCMS if present on Mars.

1. Introduction

Mars remains a key target of astrobiological interest since its past environmental conditions are thought to have been more favorable for the emergence of life. Since 2004, several space missions to Mars, including the Mars Exploration Rovers Spirit and Opportunity, the Mars Express probe, the Mars Reconnaissance Orbiter, and the Phoenix lander, have provided mineralogical data that indicate a past sustained presence of liquid water on ancient Mars, probably during the first 500 million years of the planet's history (Squyres et al., 2004; Bibring et al., 2006). During this period, Mars was bombarded by asteroids, comets, and their fragments (Cottin et al., 1999; Botta and Bada, 2002; Pizzarello et al., 2006), which would have delivered organic matter, including compounds potentially useful for the emergence of a prebiotic chemistry or even the origin of martian life to the surface of the planet (Chyba and Sagan, 1992).

* Corresponding author at: LISA, Univ. Paris Diderot, Sorbonne Paris Cité, Univ. Paris Est Créteil, UMR CNRS 7583, 61 Avenue du Général de Gaule, 94010 Créteil Cedex, France.
E-mail address: fabien.stalport@lisa.u-pec.fr (F. Stalport).

0032-0633/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.pss.2012.02.010

Even if life never arose on Mars or became extinct, the cooling of Mars and the lack of extensive plate tectonic recycling may have enabled the preservation of molecular evidence of prebiotic and/or biotic activity in ancient sediments (Morrison, 2001). Future *in situ* exploration of the Mars surface will include specific experiments to detect organic molecules that may represent chemical fingerprints of a prebiotic chemistry or biological activity, past or present. Reports of organic compounds detected on Mars are limited to atmospheric methane from orbital and Earth-based observations (Formisano et al., 2004; Krasnopolsky et al., 2004; Mumma et al., 2009) and part-per-billion (ppb) levels of chlorinated methane compounds in surface regolith observed by the Viking Gas Chromatograph-Mass Spectrometers. The positive detection of chlorinated methane was originally interpreted as residual cleaning solvents (Biemann et al., 1977), and only recently reinterpreted to be products of indigenous martian organic compounds (Navarro-González et al., 2010). The presence of methane in the martian atmosphere is controversial: the first detections are contested and it appears after more recent observations did confirm its presence (Formisano et al., 2004; Krasnopolsky et al., 2004; Mumma et al., 2009). More complex non-volatile organic compounds trapped in the regolith, such as carboxylic acids or amino acids, cannot be detected remotely and will require direct *in situ* measurements of the regolith at the surface.

To date, the only *in situ* experiment devoted to the search for complex organic compounds in the martian regolith has been the Gas Chromatograph-Mass Spectrometer (GCMS) experiments of the Viking missions in 1976. In these experiments, several surface samples, collected down to approximately 10 cm depth, were heated to temperatures of up to 500 °C, and the gases released were analyzed directly by GCMS. With exception to the controversial detection of chlorinated methane, no organic molecules of martian origin were detected at the two different landing sites within the detection limits of the instruments (Biemann et al., 1976, 1977). Although, the Viking GCMS instruments did detect chloromethane and dichloromethane at part-per-billion (ppb) levels at both landing sites in the surface regolith samples, it was argued that these chlorohydrocarbons were derived from cleaning solvents used on the instrument hardware (Biemann et al., 1977). Several explanations for the lack of organics in surface materials on Mars have been proposed including the destruction of hydrocarbons by UV and ionizing radiation (Oro and Holzer, 1979; Stoker and Bullock, 1997; Ten Kate et al., 2005; Dartnell et al., 2007; Stalport et al., 2008, 2009, 2010) and/or other oxidation processes (Chun et al., 1978; Pang et al., 1982; Yen et al., 2000; Clancy et al., 2004; Encrenaz et al., 2004). Recent *in situ* data obtained from the Northern polar region of Mars by the *Phoenix* mission showing high concentrations of magnesium perchlorate (Hecht et al., 2009), and laboratory thermal-volatilization GCMS measurements of Atacama Desert soils containing perchlorate suggest that a significant amount of organic carbon in the martian regolith (up to part-per-million levels) may have been converted to chlorohydrocarbons during high-temperature pyrolysis (up to 500 °C). This mechanism suggests the possible presence of perchlorates in the soils analyzed by *Viking* (Navarro-González et al., 2010). It has also been suggested that significant amounts of non-volatile products such as amino acids and carboxylic acids, would not have been extracted by the Viking pyrolysis procedure or would have been destroyed prior to GCMS detection (Glavin et al., 2001; Benner et al., 2000). Therefore, future GCMS analyses of complex organic compounds on Mars may require lower-temperature extraction protocols, such as chemical derivatization, that can transform less volatile and less thermally stable organic compounds into molecules that can be readily detected (Meunier et al., 2007; Buch et al., 2009).

NASA and ESA are planning a series of new robotic missions to Mars and other destinations that will incorporate *in situ* wet chemistry experiments. Chemical derivatization using dimethylformamide-dimethylacetal (DMF-DMA) has already been incorporated into the Cometary Sampling and Composition (COSAC) evolved gas experiment on ESA's Rosetta Lander and will provide amino acid detection and enantiomeric measurements on the surface of comet 67P/Churyumov-Gerasimenko in 2014 (Meierhenrich et al., 2001; Szopa et al., 2003; Goesmann et al., 2007). The use of multiple chemical derivatization agents including MTBSTFA and DMF/DMA are also under consideration for inclusion in the Mars Organic Molecule Analyzer (MOMA) instrument on the 2018 ExoMars rover mission (Buch et al., 2009). The NASA Mars Science Laboratory (MSL) mission, which is scheduled to land on Mars in August 2012, is carrying the Sample Analysis at Mars (SAM), instrument suite designed to detect a wide range of chemical biosignatures, organic and inorganic, that could provide evidence of a habitable environment and possibly signs of life (Cabane et al., 2004; Mahaffy et al., 2010). The SAM instrument suite includes a gas chromatograph quadrupole mass spectrometer (GCMS) that will enable the separation and direct analysis of volatile species present in the atmosphere or released from solid samples heated up to 1000 °C. In addition, SAM will employ a lower temperature (≤ 300 °C) chemical extraction and derivatization step using sealed metal cups filled with a mixture of MTBSTFA and DMF that will target less volatile and less-thermally stable organic compounds such as amino acids and carboxylic acids that cannot be readily extracted and detected by high-temperature pyrolysis and GCMS analysis alone.

MTBSTFA was originally selected as a derivatizing agent for the SAM wet chemistry experiment since the reaction can occur in a single step (Knapp, 1979), MTBSTFA is less susceptible to hydrolysis compared to other reagents, and it does not require separation of the derivatives prior to GC analysis. In addition, MTBSTFA will rapidly react with a wide range of organic compounds with acidic hydrogen atoms including amino acids, carboxylic acids, nucleobases, primary and secondary amines, alcohols, and amides (Buch et al., 2006). Furthermore, the derivatization yields for pure amino acid and carboxylic acid standards are high and typically in the range 90–100% (Rodier et al., 2001). SAM also has the ability to extract and detect higher molecular weight organic matter, including fatty acids, by thermochemolysis at temperatures >340 °C using tetramethylammonium hydroxide (TMAH). Thermochemolysis was not investigated in this study, but TMAH protocols and experiments have been tested previously using Mars analog materials from the Atacama Desert (Geffroy-Rodier et al., 2009).

Here we report the first GCMS results of amino and carboxylic acids that were extracted from a suite of terrestrial Mars analog materials using a derivatization test-bed that approximates the front-end extraction capabilities of the SAM flight instrument model. MTBSTFA derivatization experiments were not run using the actual SAM flight instrument model to avoid contamination of the flight instrument by the analog materials and derivatization agents themselves. The primary goal of this study was to understand the influence of minerals on the efficiency of MTBSTFA derivatization of amino and carboxylic acids using the SAM one-pot extraction approach. Since SAM hardware components were not available for this study, we did not focus on optimization of the derivatization process that will be used on Mars by SAM which will be done on the SAM testbed instrument when it becomes available. The experimental results described here will be used to guide SAM testbed derivatization operations, help formulate a sample selection strategy for the SAM derivatization experiment on Mars, and enable a more accurate interpretation of the *in situ* derivatization GCMS results obtained by SAM.