

# Extraction of amino acids from soils close to the Mars Desert Research Station (MDRS), Utah

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**Abstract:** Future space missions that aim to detect life should search for molecules that are vital to all living organisms. Although the Viking landers did not find any signs of organic molecules on Mars, signatures of past and/or present life may still exist in the Martian regolith. In this paper, we describe amino acid analyses performed in several Martian analogue soil samples collected close to the Mars Desert Research Station (MDRS), Utah, during the International Lunar Exploration Working Group (ILEWG) EuroGeoMars campaign in February 2009. The Utah desert around Hanksville is characterized as shale desert and is cold and arid with an average annual temperature of 12 °C. It is subjected to wind erosion and was shaped by fluvial erosion. The data show large differences in the total amino acid abundances between all the collected soil samples, with values ranging from non-detectable to 100 000 parts per billion (ppb). These results are explained in the context of mineralogical differences (namely different clay content) among the soil samples. The data have implications for future life-detection missions and the target mineralogy that may host biological signatures.

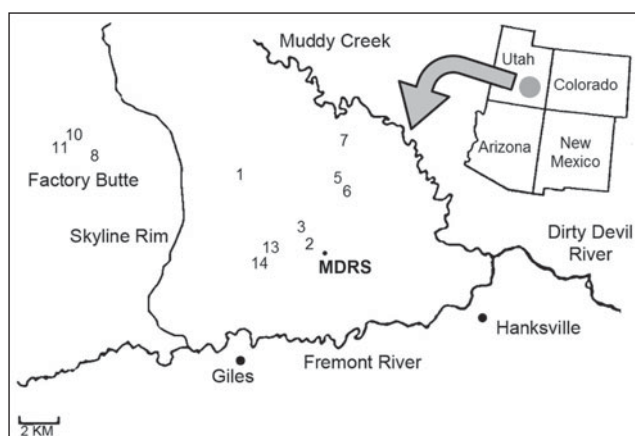
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## Introduction

The possibility of Mars harbouring life has been a fascinating topic for several centuries, and in recent decades spacecrafts have been used to investigate the past or present habitability of the Red Planet. In 1976 the Viking landers did not detect any organic compounds (representative of life on the surface) above the detection limit of a few parts per billion (ppb) (Biemann & Lavoie, 1979). This was explained by the strong UV radiation and oxidizing conditions of present-day Mars, which would destroy organic compounds (Klein, 1978; Benner *et al.* 2000; Squyres *et al.* 2004). However, when buried and shielded from exterior radiation, organic compounds are capable of surviving for geological periods of time (Kminek & Bada, 2006; Aubrey *et al.* 2006; Kanavarioti & Mancinelli, 1990). As large amounts of carbonaceous material are thought to be delivered to the surface of Mars by interplanetary dust particles (IDPs) and meteorites every year (Chyba & Sagan, 1992; Zent & McKay, 1994; Flynn, 1996; Bland & Smith, 2000), some residual extra-terrestrial organic compounds would be expected on Mars. Hence, the search for both biotic and abiotic sources of organic matter continues. In order to help prepare for future life-detection missions (such as the Mars Science Laboratory and ExoMars missions), it is necessary to perform extensive

fieldwork in terrestrial locations that resemble Mars (for a review, see Marlow *et al.* 2010). As the Martian regolith is extremely dry and the surface is depleted of organic compounds (Biemann *et al.* 1976, 1977; Biemann, 2007), terrestrial deserts have been used as Martian analogue locations. Analyses to detect organic compounds were performed in soils from the Atacama and Arequipa deserts (Skelley *et al.* 2005; Buch *et al.* 2006; Peeters *et al.* 2009), as these are two of the driest and most inhospitable places on Earth for microbial life (Navarro-González *et al.* 2003; Gómez-Silva *et al.* 2008). The present study continues the analyses of organic compounds in Martian analogue soils, and was performed on soils collected near the Mars Desert Research Station (MDRS) in the Utah desert, which receives 140 mm of annual average precipitation (Godfrey *et al.* 2008). The Utah soil displays mineralogies similar to Mars (Borst *et al.* 2010), with sedimentary deposits of sands, evaporites, clays and gypsum (Kotler *et al.* 2011). A good understanding of the interactions between the organic, mineralogical and microbial components of desert soils is crucial to determine the best locations for future space missions to Mars to be able to detect organic compounds indicative of life. Therefore, we have measured the amino acid content of Martian analogue soil samples, and related these results to the microbial and mineralogical data of the soil samples.



**Fig. 1.** Map showing the locations where the MDRS desert soil samples were collected (south-east area of Utah, USA). The right-corner inset shows the states surrounding the state of Utah (USA). Taken from Direito *et al.* (2011).

## Materials and methods

### Samples

Soil samples were collected in the period between 17 and 27 February during the 2009 EuroGeoMars campaign (Foing *et al.* 2011) from different locations near the MDRS in the south-east area of Utah (USA) (Fig. 1, Table 1). Shovels and spatulas used to collect the soil samples were sterilized by rinsing with ethanol (70%, v/v). Soil samples were then stored in sterile low-density polyethylene bags prior to amino acid analysis in the laboratory at Imperial College London. Soil samples came from several geological formations (Table 1) (Chronic 1990; Fillmore 2000). Soil samples P1, P8, P10 and P11 are from the Mancos Shale Formation (sample P1 belongs to the Tunuck Member), which was formed during the Cretaceous Period with records showing falling and rising cycles of sea level. This formation is very rich in sulphides, with some locations containing gypsum. Samples P2 to P7 are from the Morrison Formation, belonging to the late Jurassic Period. This formation contains bentonite-rich shales deposited in mudflats, with sparse units of fine-grained sandstones. Samples P13 and P14 are from the Dakota Sandstone Formation and were formed during the Cretaceous Period. They were collected from locations that contained fossils of shells in the upper layer. The soil pH and organic matter content (Orzechowska *et al.* 2011), microbial community content (Direito *et al.* 2011) and mineral composition (Kotler *et al.* 2011) were determined. A powdered sample of serpentinite (hydrated magnesium silicate), provided by the Natural History Museum Bern, was used as a procedural blank. It was heated to 500 °C for 3 h and subjected to the same amino acid experimental procedure as the soil samples.

### Chemicals and tools

All chemicals and tools were purchased from Sigma-Aldrich, except for the AG<sup>®</sup> 50W-X8 cation exchange resin (100–200 mesh, from Bio-Rad), the 1 ml V-vials (from Fisher)

**Table 1.** The MDRS desert soil samples (see Fig. 1 for location) and the corresponding coordinates, altitude, depth and formation from which they were collected

Sample name	Coordinates	Altitude (m)	Depth	Formation
P-1	N38.43621° W110.81943°	1350	Surface	Mancos Shale/Tunuck
P-2	N38.40746° W110.79280°	1382	Surface	Morrison
P-3	N38.40737° W110.79261°	1375	Surface	Morrison
P-5	N38.42638° W110.78342°	1400	Cliff	Morrison
P-6	N38.42638° W110.78342°	1400	Cliff	Morrison
P-7	N38.45424° W110.79092°	1357	Surface	Morrison
P-8	N38.43755° W110.88725°	1482	Surface	Mancos Shale
P-10	N38.43896° W110.89001°	1500	Surface	Mancos Shale
P-13	N38.40630° W110.79547°	1405	Surface	Dakota
P-14	N38.40630° W110.79547°	1405	15 cm	Dakota

and the trifluoroacetic anhydride/isopropanol (TFAA-IPA) derivatization kit (from Alltech). All the tools, glassware and ceramics used in the amino acid analysis were sterilized by wrapping in aluminium foil and placing in a furnace at 500 °C for 3 h.

### Amino acid extraction, derivatization and gas chromatography–mass spectrometry (GC-MS) analysis

Around 100 mg of each soil sample was placed inside Pyrex test tubes (16 × 150 mm) with 1 ml high-performance liquid chromatography (HPLC) grade water, flame sealed and put on a heating block at 100 °C for 24 h. After the hot-water extraction, the outsides of the tubes were rinsed with HPLC grade water before being opened; 500 µl of the supernatant of each soil sample was transferred to a smaller test tube (3 ml) and vacuum dried. Each small test tube was placed inside a Pyrex test tube containing 1 ml 6 M HCl. The Pyrex test tubes were flame sealed and placed in an oven at 150 °C for 3 h. After the acid hydrolysis, the outsides of the Pyrex tubes were rinsed with water before being opened. The small test tubes were taken out and the extracts were dried prior to the desalting step. The dried extracts were brought up in 3 ml water, desalted on a cation exchange resin and eluted with 5 ml of 2 M ammonium hydroxide. The eluates were vacuum dried, dissolved in 100 µl of water, transferred to 1 ml V-vials and dried with a flow of N<sub>2</sub>.

100 µl of an acetylchloride:isopropanol mixture (30:70, v/v) was added, and the vials were tightly capped with Teflon-lined screw caps and placed in a heating block for 1 h at 110 °C. The samples were checked 5 min into the reaction to make sure that the vials were tightly capped. After the esterification step, the vials were cooled to room temperature, and the samples were

Table 2. Amino acid peak identification in the GC-MS chromatograms of the standards, serpentine blank and Mars analogue desert soils. Molecular ions used for identification and quantification (first ion) are also displayed. Single ion *m/z* 202 was selected to identify and quantify pyrene (used as an external standard)

Peak #	Amino acid	Single ion ( <i>m/z</i> )
1	A-AIB	154
2	D-alanine	140
3	L-alanine	140
4	D,L- $\alpha$ -ABA <sup>a</sup>	154
5	D-valine	168
6	L-valine	168
7	Glycine	126
8	D,L- $\beta$ -AIB <sup>a,b</sup>	182/153
9	D-norvaline	168
10	L-norvaline	168
11	$\beta$ -alanine	168/185
12	D,L- $\beta$ -ABA <sup>a,b</sup>	140/182/153
13	D-leucine	140/182
14	L-leucine	140/182
15	D-norleucine	182/114
16	L-norleucine	182/114
17	$\gamma$ -ABA	182/154
18	D-aspartic acid	184/212
19	L-aspartic acid	184/212
20	D-glutamic acid	180/198
21	L-glutamic acid	180/198

<sup>a</sup>Optically pure standard not available for enantiomeric identification.

<sup>b</sup>Enantiomers could not be separated under the chromatographic conditions.

slowly dried with a flow of N<sub>2</sub>; 100  $\mu$ l of methylene chloride and 50  $\mu$ l of TFAA were added. The vials were tightly capped and heated at 100 °C for 10 min in a heating block. The vials were cooled to room temperature, and the samples were slowly dried with a flow of N<sub>2</sub>; 65  $\mu$ l of methylene chloride and 10  $\mu$ l of pyrene in methylene chloride (200  $\mu$ g  $\mu$ l<sup>-1</sup>), which was used as external standard, were added to the samples; 1  $\mu$ l of the sample was injected into the GC-MS system.

GC-MS analyses were performed using an Agilent 7673 series injector, 6890 network GC system and 5973 mass selective detector. Separation of the D, L-amino acid enantiomers was achieved using a Heliflex Chirasil-Val column (50 m  $\times$  0.25 mm ID  $\times$  16  $\mu$ m film thickness) from Alltech. Helium was used as carrier gas with a flow of 1 ml min<sup>-1</sup>. The injection port (splitless injection) and the MSD transfer line were set to 220 °C. The oven programme was held for 5 min at 5 °C, increased by 2 °C min<sup>-1</sup> to 80 °C and held for 5 min, increased by 1 °C min<sup>-1</sup> to 100 °C, increased by 2 °C min<sup>-1</sup> to 200 °C and held for 10 min, and finally increased by 10 °C min<sup>-1</sup> to 220 °C and held for 5 min (total run time of 104.5 min). MS quad was set to 150 °C and MS source to 230 °C. Data were analysed using the MSD ChemStation Data Analysis software package. Amino acids were identified by comparison of the retention time and mass fragmentation pattern with known amino acid standard mixtures (Table 2 and Fig. 2).

## Results and discussion

We analysed the amino acid content of several soil samples collected near the MDRS. Fig. 2 shows selected ion GC-MS chromatograms of the acid-hydrolysed hot-water extracts of the ten desert soil samples (P1–P14) and a serpentinite blank. The chromatograms were scaled to aid comparisons, with the scale factors shown in brackets. The corresponding amino acid abundances are displayed in Table 3. The most abundant amino acids were L-glutamic acid, D-glutamic acid, L-aspartic acid, L-valine, L-alanine, L-leucine and glycine (Table 3 and Fig. 2). These amino acids were also the most abundant in other hot desert soils, such as the Oman (Martins *et al.* 2007), Arequipa (top of slope sample) and Atacama (flat top hill sample) desert soil samples (Peeters *et al.* 2009). Peeters *et al.* (2009) also detected  $\beta$ -alanine and  $\gamma$ -ABA in the Atacama and Arequipa samples, which we did not detect in the MDRS soil samples.

The total amino acid abundances were very heterogeneous in the ten MDRS samples, with values ranging from no amino acids detected in soil samples P2, P5 and P6, to 100 000 ppb in sample P13 (Fig. 2 and Table 3). Sample P1 had total amino acid abundances of a few hundred ppb, samples P3, P8 and P10 contained a few thousand ppb, and samples P14 and P13 were the most abundant samples containing 17 000 and 100 000 ppb, respectively. When comparing the amino acid distribution and abundances, it is important to consider the different locations from which the soils were collected. Soil samples P5 and P6 were collected from the same location (same coordinates), samples P13 and P14 were from the same location but different depths (P13 is surface sample, while P14 is from 15 cm below the surface), and samples P8 and P10 were from the same area but with different coordinates (Fig. 1 and Table 1). P2 was collected from the same area as P3, but their total amino acid abundances are different (no amino acids were detected in sample P2). The differences in abundances between the ten soil samples may be explained by different mineral compositions, which can influence the content and stability of organic compounds in the soil (Peeters *et al.* 2009).

Analyses show that samples P5 and P6 have 23 and 33% total clay, respectively, and no detectable amino acids, while samples P13 and P14 (which are the most amino-acid-rich MDRS soil samples) have 9 and 1% total clay, respectively (Kotler *et al.* 2011). Therefore, our data indicate that soils with the higher percentage of clay are those with less extractable amino acids. Clays are expandable layers that may hold organic compounds and should protect these organic molecules against destruction by radiation and oxidizing conditions (as no radiation or oxygen penetrates the clay layers). However, once the clay layers are compacted very tightly together, organic compounds are adsorbed in the clay and it is not possible to extract the molecules. This scenario is also applicable to shales (i.e. clay-rich sedimentary rocks).

Samples P8 and P10, both from the Mancos Shale Formation, contain 4 and 5% organic matter, respectively, which are the MDRS samples that contain the highest percentage of organic matter (Orzechowska *et al.* 2011). Total amino acid





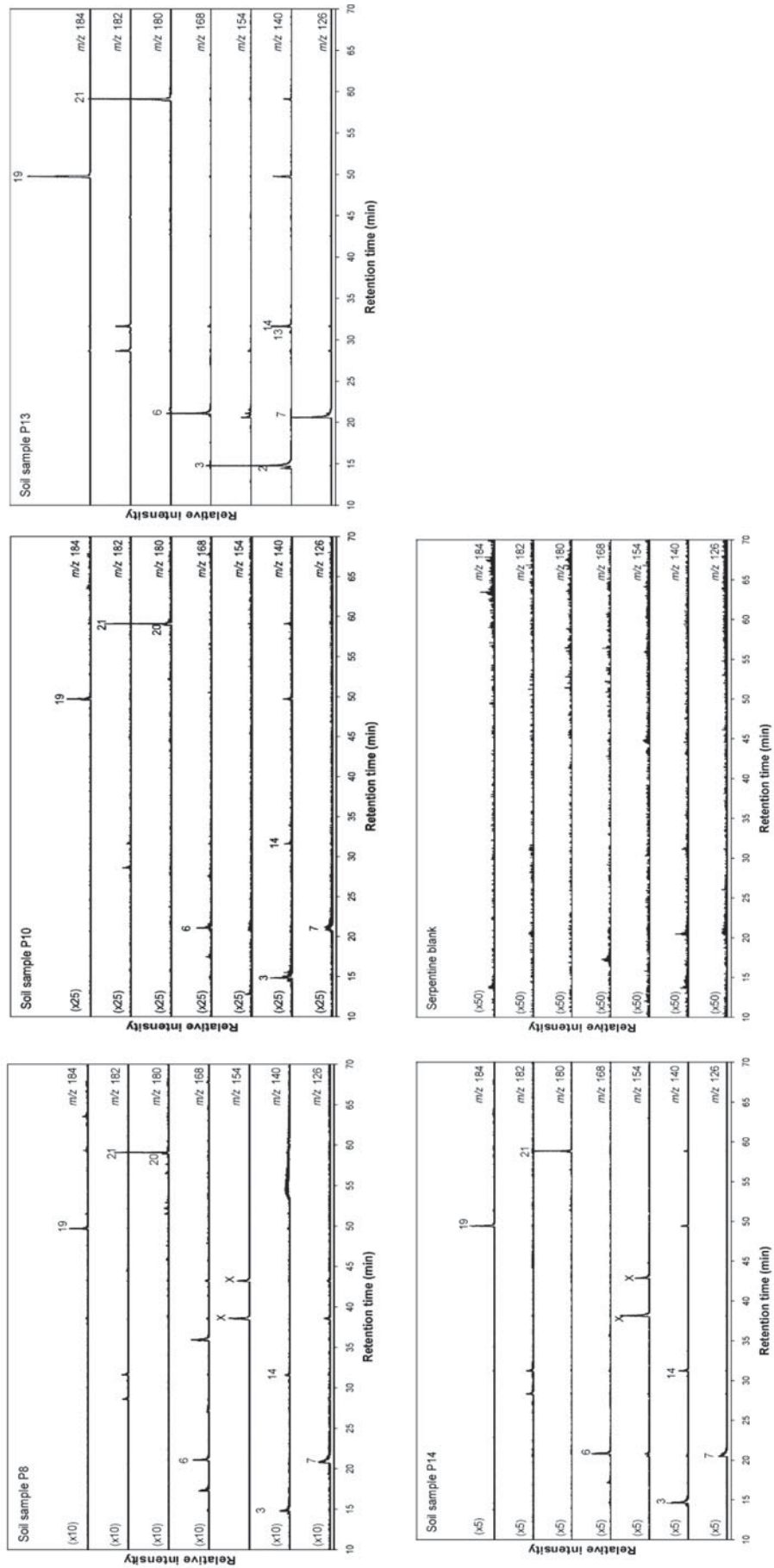


Fig. 2. (Cont.)

Table 3. Summary of the average total amino acid abundances (in ppb) in several Mars soil analogues collected in the Utah desert and measured by GC-MS<sup>a</sup>

Amino acid	P1	P2	P3	P5	P6	P7	P8	P10	P13	P14
$\alpha$ -AIB	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
D-alanine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4314 ± 216	n.d.
L-alanine	n.d.	n.d.	76 ± 3	n.d.	n.d.	n.d.	1114 ± 98	803 ± 76	32934 ± 901	5944 ± 501
D,L- $\alpha$ -ABA <sup>c</sup>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
D-valine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L-valine	n.d.	n.d.	164 ± 4	n.d.	n.d.	n.d.	783 ± 27	322 ± 16	12793 ± 484	2622 ± 307
Glycine	n.d.	n.d.	92 ± 13	n.d.	n.d.	n.d.	1324 ± 106	327 ± 24	17390 ± 531	2535 ± 548
D,L- $\beta$ -AIB <sup>b,c</sup>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
D-norvaline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L-norvaline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
$\beta$ -alanine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
D,L- $\beta$ -ABA <sup>b,c</sup>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
D-leucine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	514 ± 68	<1
L-leucine	n.d.	n.d.	47 ± 9	n.d.	n.d.	n.d.	451 ± 48	24 ± 13	12897 ± 404	2695 ± 335
D-norleucine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L-norleucine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
$\gamma$ -ABA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
D-aspartic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L-aspartic acid	83 ± 3	n.d.	102 ± 6	n.d.	n.d.	n.d.	220 ± 12	191 ± 22	7775 ± 155	1131 ± 48
D-glutamic acid	53 ± 3	n.d.	57 ± 5	n.d.	n.d.	n.d.	128 ± 5	177 ± 47	n.d.	n.d.
L-glutamic acid	139 ± 9	n.d.	194 ± 17	n.d.	n.d.	n.d.	600 ± 13	472 ± 10	10892 ± 176	1747 ± 69
Total <sup>d</sup>	280	n.d.	730	n.d.	n.d.	n.d.	4600	2300	100000	17000

<sup>a</sup>Quantification of the amino acids included background-level correction using a serpentine blank. The associated errors are based on the standard deviation of the average value between six separate measurements ( $N$ ) with a standard error,  $\delta x = \sigma x \cdot N^{-1/2}$ .

<sup>b</sup>Enantiomers could not be separated under the chromatographic conditions.

<sup>c</sup>Optically pure standard not available for enantiomeric identification.

<sup>d</sup>Total amino acid concentrations rounded to two significant digits.  
n.d., not detected.

abundances of 4600 and 2300 ppb, respectively, indicate that amino acids are also efficiently retained in these soil types or the higher organic content is due to the presence of more refractory aromatic components such as kerogen-type material. The concentration of naphthalene in samples P8 and P10 was measured to be 20 and 10 ng g<sup>-1</sup>, respectively (Orzechowska *et al.* 2011).

Although the clay content is important, other minerals should also be taken into account. Our data show that samples containing a high percentage of gypsum (calcium sulfate dehydrate), such as P14, P10 and P8 (Kotler *et al.* 2011), also have a high/medium amino acid content. This is in agreement with the results from Aubrey *et al.* (2006), who determined that amino acids can be preserved for geologically long periods in sulfate mineral matrices.

Differences in the total amino acid content in MDRS soils may also reflect the proliferation of any microbial population present. Notably, the total amino acid content follows the sequence Dakota Formation > Mancos Shale > Morrison Formation, while porosity and permeability follow the same trend. Higher permeability represents opportunities for microbial populations to access water, nitrogen and oxygen that can add to the organic matter present in the rock samples and therefore promote growth. Samples P7, P8, P10, P13 and P14 were collected after 23 February 2009 when 1 mm of rain was recorded (Foing *et al.* 2011). Except for samples P6, P7 and P14, at least one (or more) domains of life were present in the soil samples (Direito *et al.* 2011; Thiel *et al.* 2011). While we did

not detect any amino acids in soil samples P6 and P7, sample P14 had a total amino acid abundance of 17000 ppb (Table 3). Two possibilities exist to explain the differences between the amino acid and DNA data of sample soil P14: (i) The amino acids are artefacts introduced through sample handling. Further insight is provided by examining the racemic nature of the amino acids in soil sample P14. The sample contains exclusively L-amino acids reflecting the contribution of recent life. All other samples that have amino acids, and for which at least one domain of life was detected, contain a mixture of D- and L-amino acids (Table 3), indicating that racemization of the amino acids could occur over an extended period of time. (ii) Alternatively, the fact that no domain of life was detected in sample P14 is explained by zero-percent DNA recovery from a spiked P14 sample, indicating that even when a (spiked) micro-organism is present in the soil, DNA is not recovered and detected, giving a false negative (Direito *et al.* 2011).

It is also interesting to note that although bacteria were detected in soil samples P2 and P5 (Direito *et al.* 2011), we did not detect any amino acids in these soil samples (Fig. 2 and Table 3). Bacteria were detected in those two samples only with the PowerSoil kit, with no confirmation with the FastDNA kit, suggesting a false positive (Direito *et al.* 2011).

#### Implications for future life-detection missions to Mars

Multi-disciplinary studies of Mars analogue desert soils showing the interaction of organic, mineralogical and microbiological compositions are of extreme importance for future

life-detection missions to Mars. Our results show that the mineral composition of a soil can influence the content of organic compounds. As we now have a better understanding of the mineralogical composition of Mars, as found by the Mars Exploration Rovers and Mars Express mission (Chevrier & Mathé, 2007), great care must be taken when choosing target locations for organic analysis in future life-detection missions to Mars. Samples in the MDRS area show notable variation in their amino acid contents. These variations appear to reflect the ability of certain soil types to host microbial populations and effectively preserve their organic remains. The relationship between microbial and organic analysis is another important one. While microbial analysis did not detect any microorganisms in soil sample P14, our organic analysis detected present-life amino acid signatures. On the other hand, results show the presence of bacteria in two soil samples (P2 and P5) where no amino acid has been detected. Although Direito *et al.* (2011) did not determine the abundance of (potential) bacteria in these two soil samples, we know that the limit of detection of our GC-MS is 10 pg of amino acid in a sample. The Viking landers also did not detect any organic compounds on Mars above the detection limit of a few ppb (Biemann *et al.* 1976, 1977), but the Viking Labeled Release experiment established the presence of microbial activity (Levin and Straat, 1976). This was explained by the destruction of organic molecules due to intense UV flux on Mars and the highly oxidizing nature of the Martian surface (Benner *et al.* 2000; Squyres *et al.* 2004). Alternatively, it has been suggested that the Viking organic analysis instrument was not sensitive enough and could not detect the degradation products generated by several million bacterial cells per gram of Martian soil (Glavin *et al.* 2001). As preparation for future life-detection space missions, it is crucial to perform further parallel mineralogical, microbial and organic analyses of several Mars desert soil analogues, and determine the limit of detection of the experimental methods used.

## Conclusions

We have analysed the amino acid content of several Mars analogue soil samples collected near the MDRS, in Utah (USA). The results show a large variation between the soil samples, even the ones that were collected from the same location. Three soil samples (P2, P5 and P6) did not contain any amino acid, while two other samples (P13 and P14) had a high amino acid content. Our data indicate that the mineral composition of the soil strongly influences its organic composition or the extractability of organic material from the mineral matrix. Soil samples that contained a high percentage of clay did not have any detectable amino acids. This has implications for future life-detection missions to Mars, as locations with low (or absent) clay content should be targeted if we are to detect the molecular signatures of life.

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