Effects of Oxygen-Containing Salts on the Detection of Organic Biomarkers on Mars and in Terrestrial Analogue Soils

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Abstract

The detection of chlorinated hydrocarbons by Curiosity on Mars has been attributed to the presence of unidentified indigenous organic matter. Similarly, oxychlorines on Earth have been proposed to be responsible for the apparent lack of organics in the Atacama Desert. The presence of perchlorate (ClO_4^-) poses a unique challenge to the measurement of organic matter due to the oxidizing power of oxychlorines during commonly used pyrolysis-gas chromatography-mass spectrometry (py-GC-MS) methods. Here, we show that perchlorates and other oxyanion salts inhibit the detection of organic compounds, but that removing these problematic species prior to pyrolysis by using an optimal sample extraction duration and suitable ratios of water to sample mass enables analysis. We have characterized leached and unleached samples containing perchlorates from the Atacama Desert and have found that after leaching, the py-GC-MS chromatograms of the dried mineral residues show identifiable biomarkers associated with indigenous cyanobacteria. Samples which were pyrolyzed without leaching showed no detectable organic matter other than background siloxane and very weak or no trace of detectable polychlorinated benzenes Dried sample residues remaining after leaching, the mineral matrix and water-insoluble organic matter, showed a strong organic response in all cases when analyzed by py-GC-MS. These residues are most likely the product of the pyrolysis of water insoluble organics originally present in the samples. In addition, our results imply that previous soil analyses which contained high levels of oxyanions and concluded that organics were either not present, or at extremely low levels, should be re-examined.

1. Introduction

Organic compounds should be present on Mars, if for no other reason than ongoing chondritic infall (Flynn 1996). Several were detected during the first attempt in the mid-1970s by the two Viking Landers, but they were all attributed to terrestrial contamination (Biemann *et al.* 1977). Subsequently, the martian surface was viewed for several decades as containing one or more unidentified oxidants that destroyed organics (Zent and McKay 1994). In 2008, the Phoenix Mars lander analyzed the martian soil at its northern latitude landing site. The *Thermal and Evolved Gas Analyzer* (TEGA), a thermal desorption system feeding a mass spectrometer detected only CO_2 released from carbonates and no organic molecules (Boynton *et al.* 2009). The *Wet Chemistry Laboratory* (WCL) (Kounaves *et al.* 2009) performed the first wet chemical analyses of three martian soil samples, one from the surface and two from 5 cm depth. For all samples, the soil/water mixture was found to be slightly alkaline (pH ≈ 7.7), with an average electrical conductivity ≈ 1.4 mS/cm, and containing several salt species, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, and SO_4^{2-} (Kounaves *et al*. 2010a; 2010b). However, the most significant finding was that the dominant soluble form of chlorine at the Phoenix site was perchlorate (ClO_4^{-}), at a concentration of ~ 0.6 wt% ClO_4^{-} in the soil (Hecht *et al.* 2009; Kounaves *et al.* 2010a) and most likely present as a 60% $Ca(ClO_4)_2$, 40% $Mg(ClO_4)_2$ mixture (Kounaves *et al.* 2014b). Evidence for ClO_4^{-} at similar levels was subsequently also reported in the Rocknest aeolian deposit

by the *Sample Analysis at Mars* (SAM) instrument on the *Mars Science Laboratory* (MSL) rover Curiosity (Glavin *et al.* 2013; Leshin *et al.* 2013) and in the martian meteorite EETA 79001 (Kounaves *et al.* 2014a).

In addition to the ClO_4^-, the SAM instrument has also detected chloro-, dichloro-, and trichloro-methane (CH_3Cl_x, x=1-3) (Ming *et al.* 2014), chlorobenzene (C_6H_5Cl) and C_2-C_4 dichloroalkanes (Freissinet *et al.* 2015; Glavin *et al.* 2013), and more recently naphthalene which was suggested to be indicative of complex macromolecular organic matter (Eigenbrode *et al.* 2018).

Interestingly, the Viking lander's pyrolysis-gas chromatograph-mass spectrometer (py-GC-MS) had also detected traces of CH_3Cl and CH_2Cl_2. This detection had led to the recent suggestion that this may have been a result of ClO_4^- in the soil chlorinating either terrestrial organic contaminants or, if present, indigenous organics (Navarro-González *et al.* 2010).

Laboratory experiments under simulated martian conditions have shown that oxychlorines (including ClO_4^- and ClO_3^-) can be produced on Cl-bearing mineral surfaces via UV driven oxidation (Carrier and Kounaves 2015). This supports the hypothesis that not only ClO_4^-, but also ClO_3^-, are very likely ubiquitous on Mars. Recently, ClO_4^- was detected and quantified in regolith and rock samples from the Moon, and two chondrite meteorites (Jackson *et al.* 2015). Although present at orders of magnitude less than Mars, these findings suggest its ubiquitous presence in the solar system. Thus, analyses of organic compounds on Mars and elsewhere

89 in the solar system must consider the possible presence of oxychlorines,
90 especially ClO_3^- and ClO_4^-.

91 Although perchlorate is stable under ambient terrestrial and martian
92 conditions, it becomes a powerful oxidant when heated to temperatures higher
93 than about 150°C. Onset of O_2 evolution from oxychlorine decomposition in the
94 John Klein mudstone in Gale Crater was ~ 150°C (Ming *et al.* 2014). Thus, the
95 pyrolysis heating used prior to GC-MS (or any other analytical combination using
96 similarly high temperatures) could destroy or transform a large fraction of the
97 organics via combustion by oxychlorines and prevent direct identification of
98 indigenous organic molecules, including potential biomarkers. One exception to
99 this would be organics trapped inside minerals or refractory materials stable at
100 temperatures above 600°C that may not be affected by the presence of
101 oxychlorine compounds that decompose at lower temperatures. For analyses in
102 the temperature range of 150-600°C, this process would have thwarted the
103 detection of organics during the thermal-based analyses on Viking and Phoenix,
104 and thus the previous interpretation of these results as an absence of organics is
105 not definitive. The MSL-SAM instrument also detected chlorinated
106 hydrocarbons, specifically chlorobenzene and C_2 to C_4 dichloroalkanes.
107 However, it is not clear whether these may have been the reaction products of
108 martian chlorine and terrestrial contaminants, or indigenous organic molecules
109 either already chlorinated or thermally decomposed in the presence of these

oxychlorine compounds (Freissinet *et al.* 2015). It has also been shown that even though organics trapped in magnesium sulfate may undergo some oxidation and sulfuration during py-GC-MS, they also protect organics from oxidation by calcium perchlorate (François *et al.* 2016).

Terrestrial-based analyses of organics prior to the recognition of the effects of perchlorate on organics may have also been misinterpreted. For example, in the core of the Atacama Desert (Chile), one of the driest places on Earth, organic carbon content and biomass fall to the lowest levels found anywhere on Earth (ca. 10^3 to 10^5 cells/g of soil), concurrent with an increase in mean residence time of soil organic carbon to tens of thousands of years (Ewing *et al.* 2008). At the same time, salt crusts formed by deliquescence provide a minimalistic habitat for survival under extremely dry conditions, colonized by communities composed of extremely resistant *Chroococcidiopsis* morphospecies of cyanobacteria and associated heterotrophic bacteria (Wierzchos *et al.* 2012).

The Atacama Desert represents a reasonable martian analogue because, as may also be the case for Mars, these salt rich crusts and soils are the only remaining habitat available for life (Davila and Schulze-Makuch 2016). Thus, when searching for biomarkers on Mars one objective should be to analyze the evaporitic, chloride-bearing rocks that may have provided (or still provide) a suitable habitat enabling photosynthetic activity and adaptation to a harsh UV and hyper-arid environment (Vitek *et al.* 2010). Since these regions on the martian

surface will most likely also contain high levels of perchlorates (Clark and Kounaves 2016) and sulfates (Gaillard *et al.* 2013), the methodology to detect organic compounds on Mars has to be adjusted for their presence, and existing analyses may need reconsideration in the same way as the Atacama results, taking the hydrologic and atmospheric history of Mars into account.

It is now clear that the use of py-GC-MS in the presence of oxychlorines poses an enormous challenge, and requires the development of methodologies that can mitigate the effect of oxychlorines and other oxyanions during pyrolysis. Recent suggestions have included the use of sacrificial molecules (Kenig *et al.* 2016), supercritical-CO_2 extraction (McCaig *et al.* 2016), laser desorption-mass spectrometry, which is currently part of *Mars Organic Molecule Analyser* (MOMA) on the ESA/ExoMars 2020 mission (Li *et al.* 2015), a polymeric anion exchange resin (von Kiparski *et al.* 2013), and interpretation via gases produced during whole rock pyrolysis (Sephton *et al.* 2014). More comprehensive development is possible for future missions, as currently these techniques have either not been successfully demonstrated or introduce high risk for planetary missions.

Here, we demonstrate the utility of removing these problematic species prior to pyrolysis by using an optimal sample extraction duration and suitable ratios of water to sample mass. We have characterized leached and unleached samples containing perchlorates and sulfates from the Atacama Desert. We have found

that after leaching, the py-GC-MS chromatograms of the dried mineral residues show identifiable biomarkers associated with cyanobacteria present in this environment (Biller *et al.* 2015).

2. Site and Sample Description

2.1 Site description

The samples used in this study were collected from the Antofagasta Region of the Atacama Desert (Chile) and which have already been extensively characterized in terms of soil habitability, biomolecules indicative of potentially active cells, situ replication rates of genomes, and microbial community patterns specific to soil parameters and depths (Schulze-Makuch *et al.* 2018). The Atacama's arid to hyperarid environment renders it inhospitable, not only to macroscopic primary producers, but also limits the few microbial photosynthetic communities found there (Warren-Rhodes *et al.* 2006), mainly specialized endolithic cyanobacteria in salt outcrops (Wierzchos *et al.* 2006) and subsurface microbial communities (Fletcher *et al.* 2011). More importantly, in addition to widespread areas covered with evaporitic halite, these arid soils contain high levels of oxyanions, especially perchlorates, sulfates, and nitrates (Perez-Fodich *et al.* 2014). The Atacama Desert is considered to be a good analogue site for Mars' environment during its late Hesperian and early Amazonian epochs (Fairen *et al.* 2010).

The soil and rock samples were collected from three sites, all approximately 55-85 km east of Antofagasta: (1) Red Sands (RS: 24° 6.041' S, 70° 7.733' W); (2) Lomas Bayas (LB: 23° 23.596' S, 69° 36.237' W); and (3) Yungay (YU: 24° 5.296' S, 69° 59.673' W). The LB and YU sites are considered to be part of the hyperarid core of the Atacama Desert, while RS is part of the arid region. A map and images of the sampling sites are available as supplementary information to Schulze-Makuch *et al.* 2018.

2.2 Sample collection descriptions

At the RS and LB sites the top layer of desert pavement rocks was removed and a surface sample was taken from 0-5 cm depth. At the YU site, samples were collected from two faces of the pit. One set of samples were collected every 5 cm to a depth of 100 cm to be used for the leaching ratio analysis. A subset of these high resolution samples collected at depths of 25, 60, 75, and 85 cm were for the efficiency analyses. The other set of samples from an adjacent face were collected at depths of 0-5, 20-30, 50, and 100 cm to be used for the organic compound analyses. The RS, LB, and YU (50 cm depth) samples were selected to represent "salt poor", "sulfate rich", and "oxyanion/salt rich" environments, respectively, all appearing to contain low levels of organics when studied using standard py-GC-MS of raw samples, consistent with previous work in this area (Ewing *et al.* 2008).

A rock sample was collected from the surface ~ 2 km from the YU site. Its exposed surfaces contained partially visible grayish-green streaks. A sample of the relatively pure endolithic cyanobacteria was physically removed from a layer on the rock for analysis. Previous analyses have shown these layers to be composed of endolithic photosynthetic bacteria belonging to the genus *Chroococcidiopsis*, an extremely resistant morphospecies of cyanobacteria (Wierzchos *et al.* 2006). The cyanobacteria sample was analyzed based on the assumption that organics in the other Atacama soil samples may have significant contributions from the growth and death of such endolithic organisms.

3. Methods

The soil was sieved to remove pebbles < 2 mm and homogenized using a mortar and pestle to < 75 µm. For each sample, 1.0 g of homogenized soil was leached with Nanopure® 18.2 MΩ-cm water for 1 hour with gentle stirring. The leachate was then removed and filtered using a 0.2 µm PTFE filter. Samples prepared for ClO_4^- leaching ratio analysis were leached at a 1:5, 1:10, and 1:25 (w/v) ratio. Based on the homogeneity of the leaching ratio analyses, the samples for the ClO_4^- leaching efficacy and the inorganic anion and cation analyses were only leached at a 1:10 (w/v) ratio and diluted to a conductivity of ~ 50 µS/cm. The air dried residue from the 1:10 leached soil was then used for further analyses by py-GC-MS for organic content. The time between leaching and py-GC-MS was about 2 days. Samples were stored in clean vials in light-proof boxes in the

213 climate-controlled lab. It was assumed there would be contamination from the
214 various plastic storage containers, but none was ever observed either because
215 there wasn't sufficient transfer or the perchlorate destroyed all of it.

216 Each single leach was analyzed in triplicate for soluble inorganic content by
217 ion chromatography (IC) using a Dionex ICS-2000 Reagent Free™ IC equipped
218 with suppressed electrical conductivity detection. For separation and detection of
219 perchlorate we used a 100 μL injection volume, a Dionex AS16 Ionpac analytical
220 column with 35 mM potassium hydroxide (KOH) eluent at a flow rate of 1.25
221 mL/min, and a suppressor current of 100 μS. For anions we used a 25 μL
222 injection volume, an AS18 column with 20 mM KOH at a flow rate of 1.0
223 mL/min, and suppressor current of 75 μS. For cations, we used a 25 μL injection
224 volume, a CS12 column with 23 mM methyl sulfonic acid at 1.0 mL/min, and
225 suppressor current of 59 μS.

226 *3.1 Organic compound analysis by py-GC-MS*

227 Organic compound analyses by py-GC-MS were performed by placing a ~10
228 mg powdered sample in quartz pyrolysis tubes held in place by quartz wool. The
229 pyrolysis tubes were placed inside the platinum coil of a CDS 5200 pyroprobe
230 under helium and heated at a rate of 20°C ms^{-1} to the target temperature of 650°C
231 where it was held for 15 seconds. Although these conditions were different than
232 those used with the MSL-SAM instrument on Mars (35°C/min up to 835°C under
233 30 mbar He), the overall results should be similar. The pyrolysis unit was

coupled to an Agilent Technologies 6890 gas chromatograph using split injection at a 10:1 split ratio and an inlet temperature of 250°C. Separation was performed on a 30 m J&W Scientific DB-5MS Ultra Inert column. The GC-MS oven temperature program comprised of a start temperature of 40°C held for 2 minute, followed by a ramp of 7.5°C min^{-1} to 310°C where the temperature was held for 10 min. Helium column flow was 1.1 ml min^{-1}. Post-separation compound identification took place using an Agilent 5973 inert Mass Selective Detector, which collected data over a scan range of $m/z = 50$ to 550. Assignments are made by considering the elution order against published work and comparing mass spectra against a standard library (NIST08).

In addition to instrumental blanks, we also pyrolyzed procedural blanks from the ion chromatography consisting of an aliquot of clean quartz sand and an aliquot of quartz sand after it had been subjected to the leaching procedure.

4. Results

3.1 Effects of leaching ratio on perchlorate concentration

The ClO_4^- ion salts are highly soluble and thus can easily be leached from most samples. The samples collected every 5 cm to a depth of 100 cm were used to understand the effects of the leaching ratio. The results, shown in **Figure 1**, indicate that there was no significant difference in the concentration of recovered

253 ClO_4^- between the 1:5, 1:10, and 1:25 leaching ratios. Minor differences are
254 likely due to sample composition rather than leaching ratio.

255 *3.2 Efficacy of perchlorate leaching*

256 To confirm the efficacy of the leaching method for the ClO_4^- in the samples, a
257 set of leaching efficacy analyses were performed using a subset of representative
258 YU pit samples collected at depths of 25, 60, 75, and 85 cm. Two samples from
259 each depth were used to provide an indication for the homogeneity of the sample
260 sizes used. The samples were leached at soil:water ratios of 1:10 and the
261 concentration of ClO_4^- in each measured using IC. The air dried residues from the
262 1:10 leach were leached a second time and the remaining concentrations
263 measured. The results (**Figure 2** and **Table 1**) showed that 7-10% of the initial
264 perchlorate remained in the samples after the first leaching. This corresponds to
265 the volume of leachate that remained in the sample after filtration, and thus
266 provided the basis for estimating the residual perchlorate remaining in the
267 samples that were analyzed by py-GC-MS for organic compounds.

268 *3.3 IC analysis of all salts present*

269 The IC analyses of the leachate from the three soil samples showed
270 similarities in the patterns of salts present, but with order-of-magnitude
271 differences in concentrations. As can be seen in **Figure 3** and **Table 2**, the
272 dominant anion in all samples is sulfate (SO_4^{2-}), but is ~ 100 times greater in both

the hyperarid LB and YU samples than the RS sample. The same is also true for the apparent SO_4^{2-} parent salts, with the LB and YU soils potentially containing ~ 100 times more $CaSO_4$ than the RS soils. However, in the LB soil the $CaSO_4$ also dominates all other salts by two orders of magnitude.

3.4 Organic compound analysis by py-GC-MS

Samples which were pyrolyzed without leaching showed no detectable organic matter other than background siloxane (**Figure 4a-d**) and very weak (YU) or no trace of detectable polychlorinated benzenes (**Figure 5a-b**). The significant excess in column bleed (siloxane) with the YU sample is likely due to the interaction of the pyrolyzed perchlorate with the column, rather than the column itself.

Dried sample residues left over after leaching for IC analysis (i.e., the mineral matrix and water-insoluble organic material) were pyrolyzed and showed a strong organic response in all cases (**Figures 4e-h, 5c-d**). These residues are most likely the product of the pyrolysis of water insoluble organics originally present in the samples. For purposes of comparison, **Figure 4** also shows the results for a sample containing endolithic cyanobacteria from the Atacama Desert that was pyrolyzed after leaching. The unleached sample was not analyzed due to methodological difficulties. Alkanes, alkenes, furfural and benzonitrile were present in the cyanobacteria sample in similar distributions, although the signal was stronger as would be expected. No organics were detected from the

294 procedural blank from leaching and the quartz sand source material (data not
295 shown). The total ionic current (TIC) chromatograms were analyzed for three
296 categories of organic molecules relating to biomarkers, all of which were detected
297 in the leached samples, none of which were detected in the sample prior to
298 leaching. The extracted-ion chromatograms (XIC) showed: alkenes (*m/z* = 55)
299 and alkanes (*m/z* = 57) which are indicative of fragmentation of a biopolymer,
300 possibly from the cell wall or polymerized fatty acids (**Figure 4b,f**); furfural (*m/z*
301 = 96) and aldehydes (*m/z*=105, not shown) are indicators of carbohydrates
302 (**Figure 4c,g**); and benzonitrile (*m/z* = 103), which is a product of protein
303 breakdown (**Figure 4d,h**).

304 The extracted-ion chromatograms (XIC) (**Figure 5b,d**) show Cl_1 to Cl_6-
305 benzenes (*m/z* = 112, 146, 180, 216, 250, 284) detected in the post-leaching
306 sample residues. Since the perchlorates and other highly soluble salts were
307 extracted prior to pyrolysis, these chlorobenzenes were most likely indigenous to
308 the samples, as either atmospherically deposited polychlorinated benzene (PCB)
309 contaminates or products formed during possible reactions of indigenous organics
310 with intermediaries formed during UV production of perchlorate (Carrier and
311 Kounaves 2015). These results are in contrast to the MSL results, where it was
312 argued that chlorobenzenes were formed as a reaction product between
313 perchlorates and benzene carboxylates during pyrolysis (Freissinet *et al*. 2015).

Biogenic organic matter is known to be composed predominantly of macromolecules which are insoluble in water (Killops and Killops 2005; Tissot and Welte 1984). Given the low amount of organic material in the original samples and the small uptake expected, the organic content of the leachate is likely to be below the detection limits of py-GC-MS. Leaching the samples a second time and analyzing the leachate with UV-fluorescence also showed no signal at the 1 ppm level using humic acid as a standard.

5. Discussion

Experiments which tested the efficacy of the leaching procedure showed that this method does not necessarily remove all of the inorganic ions from a sample (**Figures S1-S3**). However, for the samples shown in **Table 3** the presence of identifiable peaks in the py-GC-MS chromatogram of the post-leaching sample (**Figures 4 and 5**) indicates that the ionic species present no longer result in complete destruction of the organic content of the sample, resulting in meaningful py-GC-MS data from which conclusions may be drawn about the source of the organic material.

Recent work to establish the minimum mass ratio (MMR) of organic carbon to perchlorate for incomplete combustion during thermal decomposition indicates that there needs to be at least 3-6× as much organic carbon as ClO_4^- by weight or 46-95 moles of carbon for each mole of ClO_4^- (Royle *et al.*, 2018). This generally agrees with the results of this study. The ratios for our samples determined using

IC for the oxyanions and TOC for the organic carbon were below this cutoff range **(Table 3)**. Post-leaching it would be expected that (with extraction efficiency ≈ 7%) the LB and RS samples would yield detectable organic molecules but YU would not, since its ratio still falls below that necessary for detection, 18.5, 540, and 2.4, respectively. However, all three samples yielded detectable organics post-leaching. This may be due to sample heterogeneity, or to the fact that the natural sample contains a mixture of salts and other oxidizing materials which decreases the MMR for organic carbon.

Figure 3 shows the challenges that will be faced measuring organic compounds in martian soil. In comparing the levels of salts between the Atacama and the Mars Phoenix sites, it is clear that even though most of the cations and anions in the martian soil are similar to those in the Yungay, there is one glaring difference. For Mars the concentration of NO_3^- is an order of magnitude lower, and the ClO_4^- and ClO_3^- are almost 3 orders of magnitude higher. With ClO_4^- being the dominant species of the oxidizing anions on Mars, this implies that the level of organic compounds will need to be at least ~ 3-6 times that of the perchlorate, or ~1800-3600 ppm to allow for a typical py-GC-MS detection.

Despite there being no measurable ClO_4^- present at either the Red Sands or Lomas Bayas samples, no organics were detected before leaching. This shows that the other oxyanion salts present, (i.e., sulfates, nitrates, chlorates, phosphates) may also have oxidative effects and can obfuscate organic molecule detection

during thermal decomposition. While it would not normally be expected that the sulfate and phosphate salts would break down and contribute oxygen at the pyrolysis temperatures used, it is otherwise problematic to explain the non-detection of organic species in the unleached samples. When mixed with other phases the onset of thermal decomposition temperature of a number of sulfates has been shown to drop to well below the temperatures used in this study (Mu and Perlmutter, 1981; McAdam *et al*., 2016; Sutter *et al*., 2017). In these natural soil samples there is likely a mixture of phases, such as metal-oxides and carbon, which have this known catalytic effect on the sulfates (Mu and Perlmutter, 1981) and a similar effect may be expected on the other salts present. Thus, the amount of oxygen available for combustion of organic carbon increases, even in samples low in perchlorates. Other than perchlorates, only sulfates have so far been examined in any detail (Lewis *et al.* 2018; Lewis *et al.* 2015).

Considering these findings and the solubility of perchlorate salts in water, future missions to detect organic matter on Mars must aim for sites with evidence of water activity. Since ClO_4^- (and NO_3^-) is highly soluble and thus a marker of liquid water, this may be an indication that the area may have been subjected to "recent" water flow. At the same time, ancient surface or near-surface water flow may have concentrated organic compounds downslope while simultaneously leaching away the perchlorate and other soluble oxyanion salts, thus efforts should focus on analyzing fluvial/lacustrine sediments and especially those sites

where there is evidence for post-depositional aqueous activity such as the lower Murray mudstone (Yen *et al*., 2017) . This is the one locality where complex, non-chlorinated organic molecules have been detected on Mars (Eigenbrode *et al*., 2018) and these sediments have also yielded some of the lowest concentrations of perchlorate yet measured in the Martian near surface sediments (Sutter *et al.*, 2017). It is thus hypothesized that aqueous flow through the Murray mudstone has leached the soluble perchlorate out of the sediments, making the organic matter preserved within this unit more amenable to detection via the thermal decomposition technique used by SAM. This is in contrast to the other unit in which 'indigenous' organic molecules have been detected in on Mars by SAM, the Sheepbed mudstone. In the Sheepbed mudstone, only simple chlorinated organic molecules have been reported, suggesting oxychlorines are having a deleterious and obfuscatory effect on the detection of organic matter (Freissenet *et al.*, 2015). The Sheepbed mudstone appears to have a similar depositional setting to the Murray (at least superficially), however, it does not show the same level of evidence for extensive late-stage fluid flow and aqueous alteration as the Murray and consequently contains perchlorate levels approximately 10× higher. Areas of recent subsurface or surface water, such as above near-surface aquifers, near exposed water-ice and downslope of recurring slope lineae (if they are in fact deliquescing-brine-induced (Chevrier and Rivera-Valentin 2012; McEwen et al. 2011, Dundas and McEwen 2015)), could also be attractive targets in the search

for organic molecules. However, these current or recent 'hydrous' areas are the most likely to be capable of supporting Earth-like microbial life and are thus designated 'Special Regions', presenting stringent planetary protection issues if they are to be explored (Kminek and Rummel 2015; Rummel *et al.* 2014).

6. Conclusions

Our findings demonstrate that by reducing the salt content of the sample with water, we counter the effects of pyrolyzing in the presence of oxychlorines and thus biologically derived organic material is readily identifiable. Since py-GC-MS is a standard analytical technique for detecting and identifying organic compounds and biomarkers on Mars and Earth, it is clear that its use in the presence of oxyanions, and especially perchlorates, will pose enormous challenges unless their oxidizing effects can be mitigated. We have shown that simple removal of perchlorate prior to pyrolysis using an aqueous extraction method allows for the identification of organic compounds reflective of biological activity. In addition, our results have shown that previous soil analyses which contained high levels of oxyanions and concluded that organics were either not present, or at extremely low levels, should be re-examined.

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Author Disclosure Statement

No competing financial interests exist for any of the authors.

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Tables

Table 1. Sample preparation data for leaching efficiency experiments. Initial leaching volume was 10 mL. Recovered volume from Leach-1 was used to calculate the expected concentration remaining in Leach-2.

Sample	*Mass (g ± 0.5 mg)*	*Recovered Volume (mL ± 5 µL)*		*Avg. Concentration (ppb ± 5%)*		*Leaching Efficiency %*
		Leach-1	*Leach-2*	*Leach-1*	*Leach-2*	
Y1-25	1.042	9	9.4	26.3	< 5	100%
Y2-25	1.047	9	9.2	21.2	< 5	100%
Y1-60	1.030	9	9.2	176.4	12.8	93%
Y2-60	1.026	9	9.6	186.9	12.6	93%
Y1-75	1.039	9	9.4	258.9	16.4	94%
Y2-75	1.047	9	9.2	148.4	10.6	93%
Y1-85	1.019	9	9.2	423.3	21.9	95%
Y2-85	1.029	9	9.2	322.3	32.1	90%

Table 2. Inorganic composition of the Atacama samples as determined by ion chromatography. The RS and LB samples were taken from 0-5 cm depth and the YU samples from 50 cm depth. These samples were selected to represent "salt poor", "sulfate rich", and "oxyanion/salt rich" environments, respectively. Average (n=3) concentration of detectable species in soil reported as mg/kg. Addition data for the other Yungay depths is shown in **Table S1** in Supporting Information.

Ion Species	*Sampling Site*		
	Red Sands (RS) mg/kg	*Lomas Bayas (LB) mg/kg*	*Yungay (YU) mg/kg*
Na^+	31.4±0.2	82±14	4,937±115
K^+	22.4±0.1	98±4	785±14
Mg^{2+}	3.04±0.08	39.2±0.1	1,831±4
Ca^{2+}	11.2±0.8	5,148±67	3,521±128
Cl^-	1.86±0.05	12±6	3,357±4
SO_4^{2-}	101±1	12,810±221	13,981±20
NO_3^-	5.5±0.1	63±30	5,681±70
PO_4^{3-}	4.15±0.07	< 31	< 8
ClO_3^-	< 0.37	< 18	63±2
ClO_4^-	< 0.03	< 0.03	4.6±0.1
Total Ions	182	18,200	36,000

645

646

647 **Table 3**: Total organic carbon (TOC):Total Cl, N oxyanion (Ox)-salt ratios
648 calculated using ion chromatography and TOC data (Schulze-Makuch *et al.*
649 2018), before and after leaching. The RS and LB samples were taken from 0-5 cm
650 depth and the YU samples from 0-5, 20-30, 50, and 100 cm depths. Three of the
651 samples were selected to represent "salt poor" (RS), "sulfate rich" (LB), and
652 "oxyanion/salt rich" (YU 50 cm) environments, respectively.

653

Sample Site	*TOC (mg/kg)*	*Total AOx (mg/kg)*	*Ratio TOC:AOx*	*Total AOx post leach (mg/kg)*	*Post leach Ratio TOC:AOx*
Red Sands	600	111	5.40	1.11	540
Lomas Bayas	2380	12,870	0.18	129	18.5
Yungay 0-5 cm	700	998	0.70	10	70
Yungay 20-30 cm	610	15,050	0.04	150	4.0
Yungay 50 cm	480	19,730	0.02	197	2.4
Yungay 100 cm	450	75,100	0.01	751	0.60

Figure Legends:

FIG. 1. Concentration of perchlorate in soil taken from 20 depths and analyzed using three different leaching ratios 1:5, 1:10, and 1:25 all leached for 1 hr. The % difference does not vary significantly with leaching ratio and minor differences in concentration are likely due to differences in sample composition rather than leaching ratio. The samples taken at 25, 60, 75, and 85 cm (stared), were then used for further leaching efficacy testing.

FIG. 2. Leaching efficiency for ClO_4^- for eight soil samples. Two samples were taken from each of four depths, selected to cover a broad range of concentrations. Detailed data used in this figure is provided in **Table 1**. Solid orange bars represent the concentration of ClO_4^- after the first leaching and green hatched bars after the second leaching. Error bars are the sum of the propagated uncertainty from the volume and concentration of the recovered leach and the standard deviation of three measurements. Dashed line denotes the limit of quantification (LOQ) for the ClO_4^- (2.5 ppb). Additional data for the other Yungay depths is shown in **Figure S1** in Supporting Information.

671 **FIG. 3.** Average (n=3) concentration of anions and cations in the Atacama RS,
672 LB, and YU, soil samples as determined by ion chromatography, compared with
673 those measured by the Phoenix-WCL and MSL-SAM instruments. The RS and
674 LB samples were taken from 0-5 cm depth and the YU samples from 50 cm
675 depth. .Based on these results we have designated the RS sample as "*salt poor*" (~
676 180 ppm total salts), the LB sample as "*sulfate rich*" (~ 13,000 ppm $SO_4^{=}$), and
677 the YU sample as "*oxychlorine rich*"(~ 68 ppm total ClO_4^- + ClO_3^-). However,
678 YU is also clearly "salt rich" (36,000 ppm total salts) and also "oxyanion rich"
679 with ~ 14,000 ppm $SO_4^{=}$ and 6,000 ppm NO_3^-. For Mars, the concentrations for
680 all ions, except NO_3^- and ClO_3^-, are from the Phoenix-WCL (Kounaves *et al.*
681 2010a; 2010b). The data for NO_3^- and ClO_3^- are estimates from both the Phoenix-
682 WCL, the Mars EETA79001 meteorite (Kounaves *et al*. 2014a), and the MSL-
683 SAM (Stern *et al*. 2017; 2015).

684 **FIG 4.** Total ion current (TIC) chromatograms showing qualitative data for
685 unleached (a-d) and leached (e-h) 50 cm depth soil and rock cyanobacteria
686 samples. The TIC of the unleached samples contains only analytical artifacts
687 (siloxanes; indicated with *) where the TIC of the leached samples contain
688 numerous peaks. Extracted-ion chromatograms (XIC) included (b, f) alkanes and
689 alkenes (*m/z = 57* and *55*, respectively; alkanes are indicated by carbon number,
690 e.g. C_{17}), which are a common component of biopolymers, (c, g) furfural (*m/z* =

691 *96*), which represent carbohydrates, and (d, h) benzonitriles (u/*z = 103*), which are
692 a product of protein breakdown, where N=tetradecene. The unleached
693 cyanobacteria sample was not amenable to analysis.

694 **FIG. 5.** TIC and XIC highlighting the detection of chlorobenzenes in the (a, b)
695 unleached and (c, d) leached samples from the Atacama Desert. Cl_1-Cl_6-benzenes
696 were detected in the leached samples using *m/z=112, 146, 180, 216, 250,* and *284*.
697 (* = column bleed (siloxanes, contaminants from sampling))
698

Figures

FIG. 1.

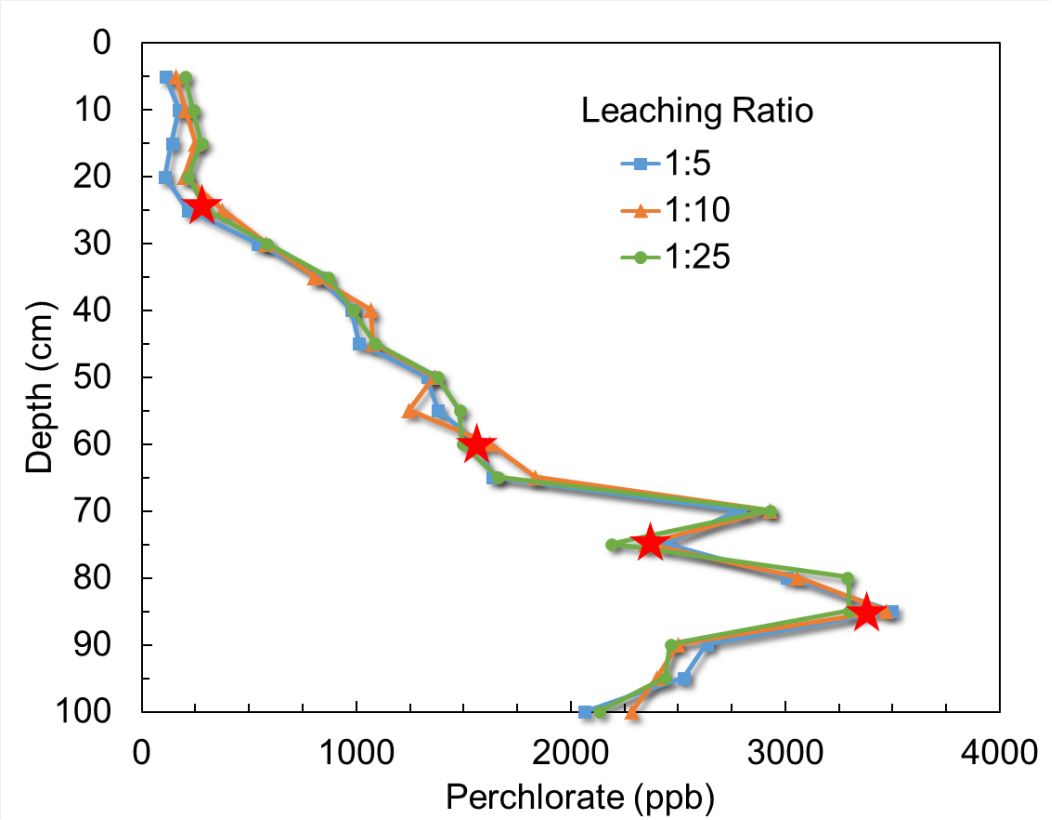
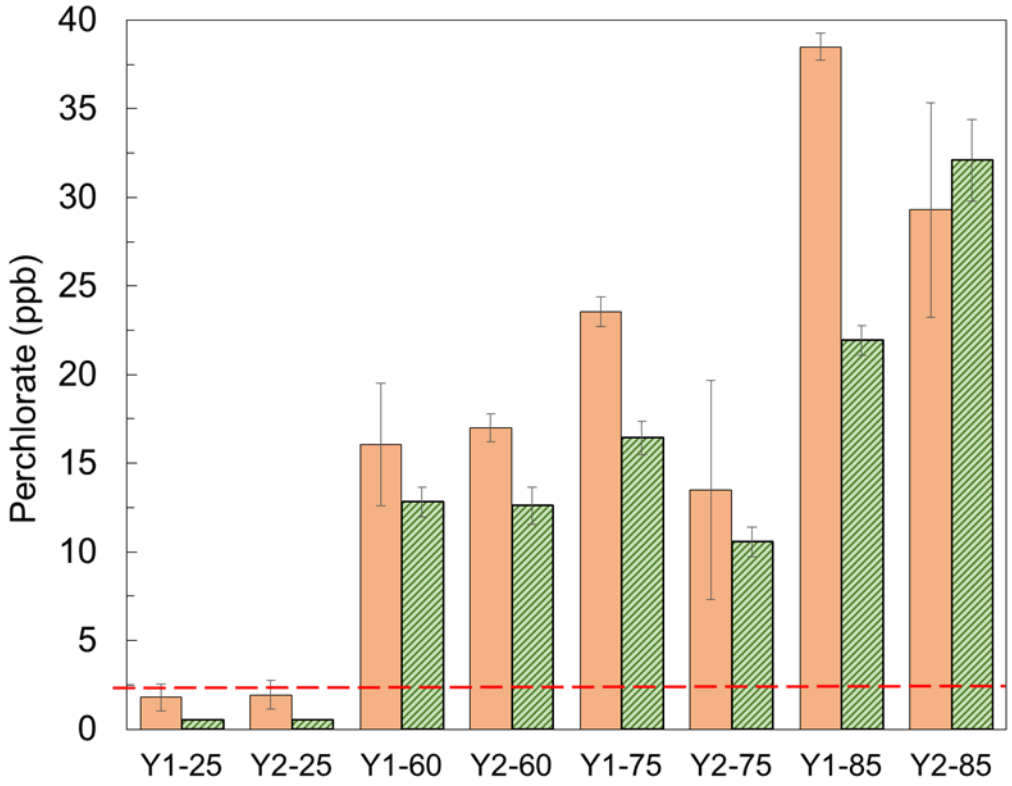
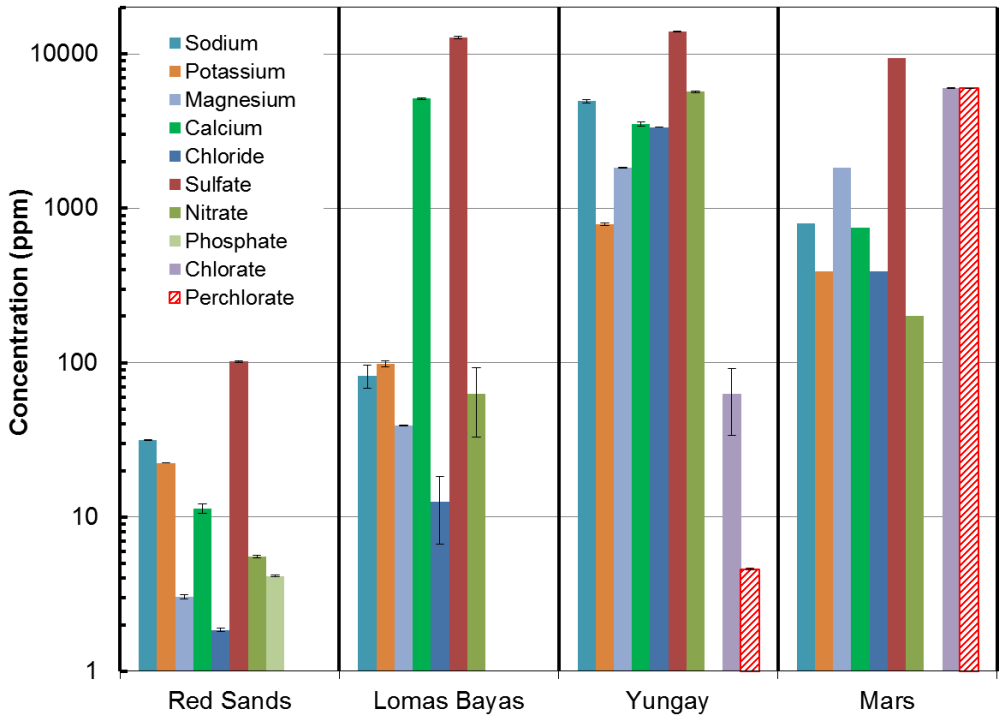


FIG. 2.


Perchlorate (ppb)
0
5
10
15
20
25
30
35
40
Y1-25
Y2-25
Y1-60
Y2-60
Y1-75
Y2-75
Y1-85
Y2-85

718

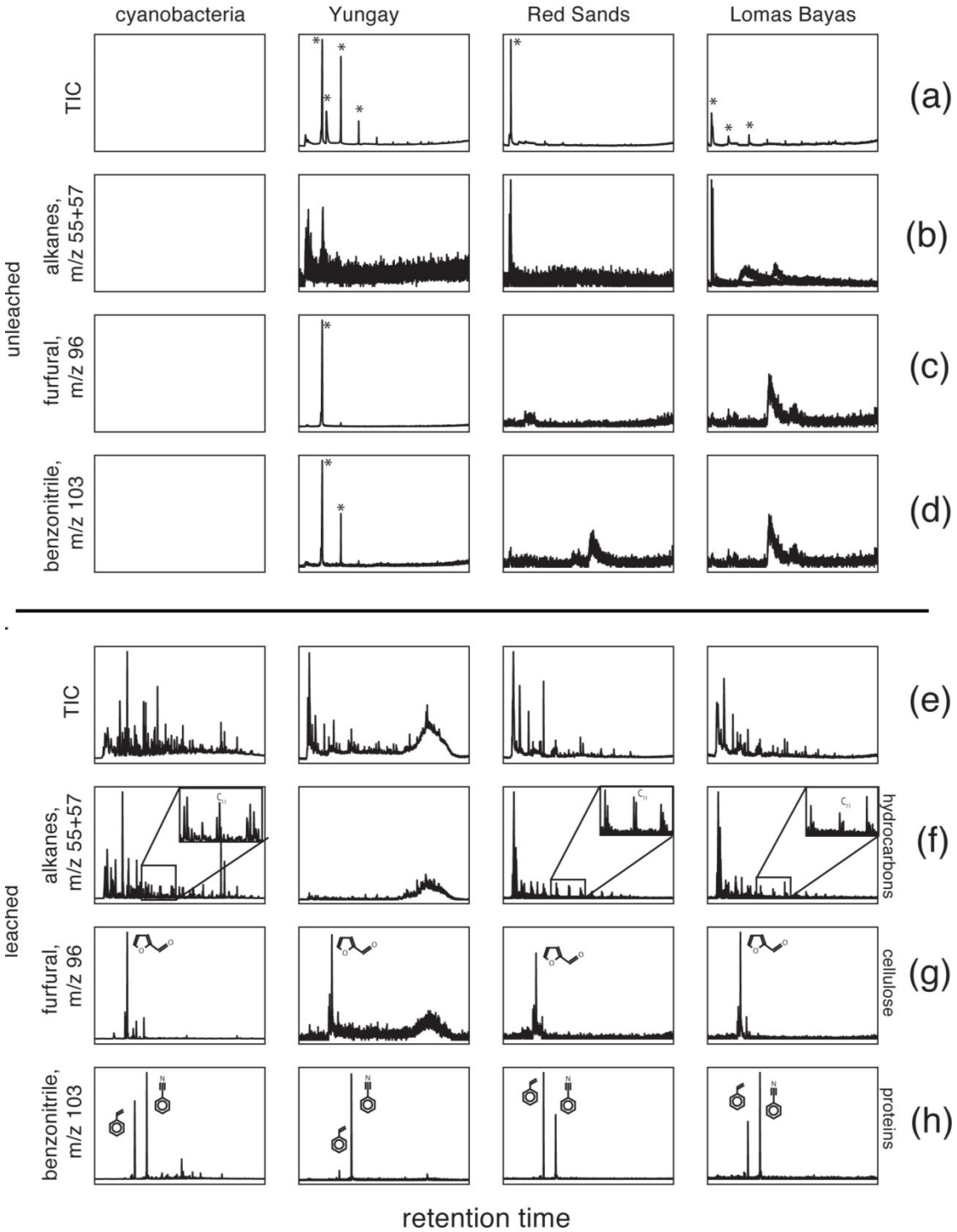
719 **FIG. 3.**



720

721

722 **FIG. 4.**

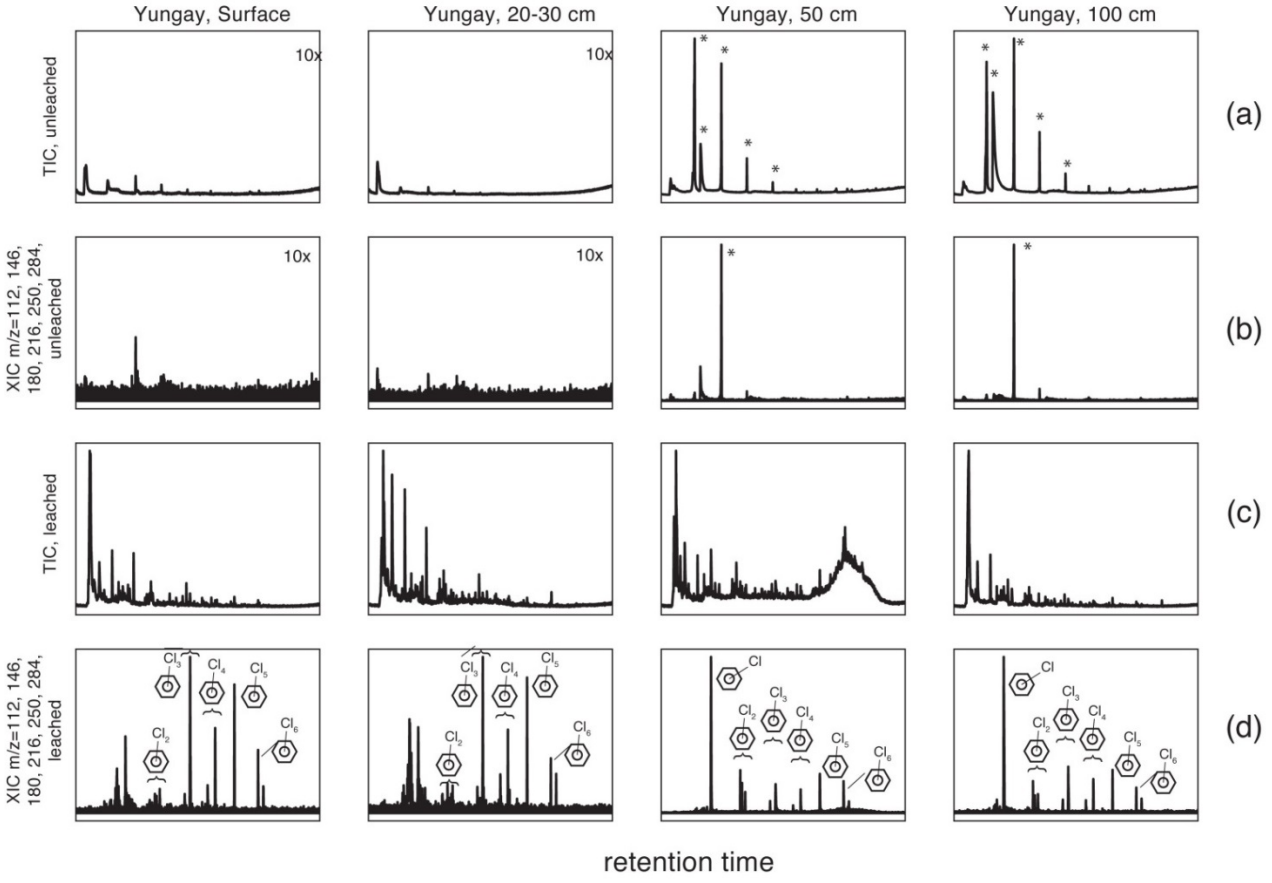

cyanobacteria
Yungay
Red Sands
Lomas Bayas
unleached
TIC
alkanes, m/z 55+57
furfural, m/z 96
benzonitrile, m/z 103
(a)
(b)
(c)
(d)
leached
TIC
alkanes, m/z 55+57
furfural, m/z 96
benzonitrile, m/z 103
(e)
(f)
(g)
(h)
hydrocarbons
cellulose
proteins
retention time

723

724 **FIG. 5.**

725

726

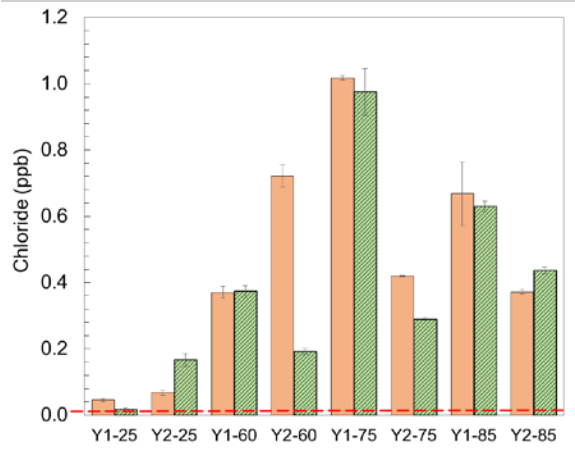


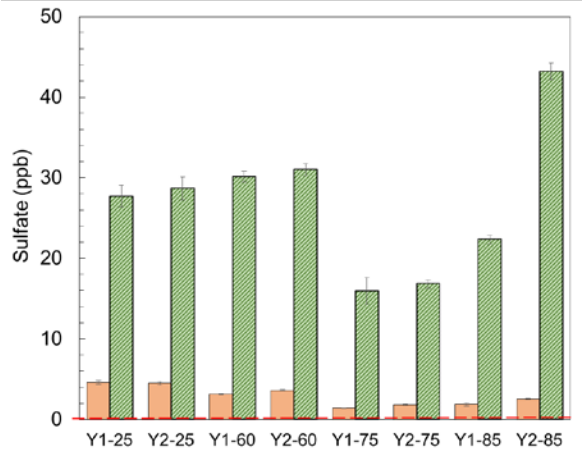
APPENDIX A - Additional Supporting Information

Table S1. Inorganic composition of the Atacama samples as determined by ion chromatography for the YU samples for 0-5, 10-30 and 100cm depths. Average (n=3) concentration of detectable species in soil reported as mg/kg.

Ion Species	*Yungay (YU) Sampling Depth*		
	0-5 cm mg/kg	*20-30 cm mg/kg*	*100 cm mg/kg*
Na^+	50.5	63.1	25,549
K^+	1,437	?	835
Mg^{2+}	46.9	62.3	1,457
Ca^{2+}	471	6,040	4,500
Cl^-	69.2	70.2	3,133
SO_4^{2-}	830	14,980	66,365
NO_3^-	88.4	68.6	5,622
PO_4^{3-}	81.3	< 3	< 3
ClO_3^-	< 0.3	< 0.3	90.0
ClO_4^-	0.039	0.114	5.20
Total Ions	3,074	21,284	107,556

740 **Figure S1.** Extraction efficiency for chloride, sulfate, and nitrate.

741 

742 

743