

Geochemical Analysis of Soils from Extreme Environments on Earth and Mars

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Abstract

Geochemical analysis of soils, including the determination of pH, salinity and organic content can provide insight into the environmental history and habitability of the region from which they are collected. This dissertation focuses on the geochemical analysis of soils from three extreme environments: the North Polar Region of Mars, the McMurdo Dry Valleys (MDV) of Antarctica, and the Atacama Desert in Chile. Also included is a novel instrument for the electrochemical analysis of Martian soils for total organic carbon.

The Wet Chemistry Laboratory (WCL) aboard the 2007 Phoenix Mars Scout Lander performed the first aqueous analysis of the Martian soil. WCL found a slightly alkaline soil dominated by soluble sulfate, perchlorate, magnesium and sodium with contributions of soluble potassium, calcium and chloride. The discovery of perchlorate on Mars suggests the presence of oxidizing chemistry in either the atmosphere or soil.

The MDV and the Atacama are good terrestrial analogs for Mars, with all three environments possessing similarities in climate and topography. Soil samples from the Atacama Desert and MDV were analyzed to determine their chemical properties. Soils in both environments exhibit similar ionic species and pH. Most interestingly, perchlorate was found at the $\mu\text{g}/\text{kg}$ level in all soils from the MDV stable upland microclimate zone. This helps strengthen the argument that perchlorate is ubiquitous on Earth and accumulates only in hyperarid regions. The chemical properties of the soils from both of these extreme environments were compared to the properties of the Martian soil as determined by WCL. Neither environment's soil was drastically different from Mars. However, the soils from the stable upland climate zone in the MDV were found to be the better terrestrial analog for the Martian soil at the Phoenix Lander site.

One vital piece of information about the soil composition on Mars has yet to be discovered, the amount of organic material present. The Mars Organic Carbon Analyzer (MOCA) is an alternative approach to determine Martian soil organic content. A prototype instrument has been developed and initial tests of its viability are described.

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GEOCHEMICAL ANALYSIS OF SOILS FROM EXTREME
ENVIRONMENTS ON EARTH AND MARS

Preface

Geochemical analysis of soils, including the determination of pH, salinity and organic content, can provide insight into the environmental history and habitability of the region from which they are collected. The abundance and diversity of life on Earth decreases as the environment becomes more extreme. Extreme environments are classified as those that are outside the boundaries of normal human living conditions. These conditions can include pH level, air pressure, temperature, salinity, radiation, dryness and oxygen level. [1] This dissertation will focus on the soils from three extreme environments: the North Polar Region of Mars, the McMurdo Dry Valleys (MDV) of Antarctica, and the Atacama Desert of Chile.

The planet Mars is an extreme environment, with its cold temperatures, high aridity and low oxygen content. Though scientists have been studying Mars for ages, little is known about the Martian soil. In fact, there is continued debate as to whether the Martian regolith can even be classified as soil.¹ [2] Between 1976 and 2011 only six Mars missions have successfully landed and performed analyses on the surface of the planet: Viking 1, Viking 2, Mars Pathfinder, MER-A Spirit, MER-B Opportunity, and most recently Phoenix. Of these six missions, Phoenix was the first to ever combine the Martian soil with water and perform analyses, which provided an abundance of new information about the Martian soil, such as soluble ion content and soil pH. The instrument which performed these analyses, the Wet Chemistry Laboratory (WCL), is the subject of Chapter 1. This opening chapter presents an overview of the WCL instrument design, followed by the instrument's C, C, and C (calibration, characterization, and cataloging) and discusses the instru-

¹For the purposes of this work, the term soil will be used. Definitions of regolith, soil and Martian soil can be found in Appendix B.

ment's findings as they stand to date.

Due to the limitations of performing *in-situ* analysis of the Martian surface, instruments destined for future missions must be rigorously tested on Earth prior to being chosen for inclusion on a mission. This ensures only instruments which are capable of providing the most reliable and complete analysis are chosen. The analysis of Martian meteorites collected on Earth provides the next best thing to direct *in-situ* analysis of the Martian soil and would be ideal for testing new instrumentation. However, due to the limited number of meteorites available for analysis, it is not practical or possible to use meteoritic material to test novel instrumentation. Instead, analog soils, which resemble as closely as possible the size, texture and composition of the soil on Mars, are used for this purpose.

Tests of the WCL were performed *in-situ* on soils from the McMurdo Dry Valleys of Antarctica as part of the 2007 International Polar Year (IPY). The MDV are fairly isolated from human activity and thus free from man-made contamination. Additionally, like Mars, the MDV are a cold, hyperarid desert and considered to be one of the best Mars analog environment on Earth. [3, 4] As is the case with most extreme environments, analysis of soils from the MDV, especially those from the upper valleys, is limited due to the lack of accessibility to these remote areas. Therefore, in addition to testing the WCL *in-situ* on MDV soils, many additional soils were collected and analyzed back in the laboratory. The analysis of MDV soils is the focus of Chapters 2 and 3. Chapter 2 provides an overview of the analysis of MDV soils for the determination of soil salinity, conductivity, and pH. Relationships and trends between pits and valleys are presented, as well as how the soils of the MDV compare to the soils on Mars at the Phoenix Lander site in terms of salinity, conductivity and pH. Chapter 3 focuses on the most surprising discovery from

this analysis the presence of a natural source of perchlorate in the MDV, particularly the upper valleys, and how this helps increase our understanding of the perchlorate formation pathway.

In addition to the soils of the MDV, soils from a second extreme environment on Earth and a Mars analog environment, the Atacama Desert, were also studied. The Atacama is another hyperarid desert but with a more moderate temperature. Many scientists have used the Atacama to study how life can survive in conditions with very little to no water and to test the next generation of instruments for Mars exploration. Chapter 4 presents an overview of the analysis of soils from three locations within the Atacama Desert for the determination of soil salinity, conductivity and pH. These soils are then compared to the soil from Mars at the Phoenix Lander site.

During the investigation into the soluble salts present in the soils of the MDV and the Atacama, it was necessary to prepare the soils for analysis by extracting the soluble salts. At this time it was discovered there is no established method for the extraction of soluble salts from extreme environment soils. Though guidelines exist as to how soil samples should be collected, stored, and analyzed, there is much variation in the literature as to the method of soil sample preparation prior to analysis. Proper sample preparation is extremely important to ensure the analysis performed is an accurate representation of what is present in the original soil sample. The need for a standardized approach to soil sample preparation is imperative to not only ensure complete analysis but also to allow for analyses, performed at different times or by different groups, to be directly comparable. This is of utmost importance when dealing with the analysis of soils from extreme environments where the number of analyses are limited. Chapter 5 highlights the necessity of standardizing soil sample preparation. Preliminary results are presented showing how sev-

eral sample preparation variables (leaching time, leaching ratio, method of agitation, and sample separation/sizing) affect the analysis results as well as a discussion outlining a proposed in-depth study into the effects of soil preparation on analysis results.

When addressing the history and habitability of an extreme environment, either on Earth or in outer space, analysis of soils for “nutrients,” in the form of soluble ionic species, is only one piece of the puzzle. It is also important to analyze for the presence of organic material. Life, as we know it on Earth, requires organic molecules. Though a wide variety of carbon-containing molecules are known to be generated abiotically in outer space, the presence of organics in the soil on Mars is still a potential indicator for past or even present life on the planet. The Viking and Phoenix missions were equipped to search for organics on Mars but none were found. This result is puzzling because even in the absence of organics produced on Mars organic compounds should still be present via meteoritic bombardment of the planet’s surface.

The focus of Chapter 6 is the analysis of soils for the presence of organic materials. Background is presented on previous analyses of extreme environments’ soils on Earth for the presence of organics as well as past and future missions to look for organics on Mars. A novel instrument for the detection of total organic carbon (TOC) on Mars, called the Mars Organic Carbon Analyzer (MOCA) is then presented. This instrument is designed to analyze the TOC present in the Martian soil, as opposed to specific organic molecules, which allows the instrument to perform an assessment of habitability and biological potential that does not depend on the presence of any specific organic molecules. The design and fabrication of MOCA is discussed as well as the testing performed to date. The current limitations of the instrument are then presented with suggestions for future work to bring the instrument from

NASA's technology readiness level (TRL) 4 to a TRL 6.

Extensive analysis of soils from extreme environments on Earth such as the MDV and Atacama Desert are paramount to increase the overall understanding of these regions which are not widely studied. Additionally, these environments are particularly important to study because these soils can and have been used as the limits of life and terrestrial analogs to Martian soil in the testing of planetary science instrumentation which can be used to increase our understanding of other planets such as Mars. Overall Conclusions proceeds to wrap up the discussion of the analysis of these extreme environment soils. The soils from all three extreme environments discussed herein are compared to determine which extreme environment on Earth, the McMurdo Dry Valleys of Antarctica or the Atacama Desert in Chile, possess soil which is a better analog to Martian soil from the northern polar region of the planet based on soil pH, conductivity and salinity.

1 Phoenix's Wet Chemical Laboratory (WCL)

1.1 Introduction

The Phoenix Mars Scout Lander launched on the 4th of August 2007 from Cape Canaveral Air Force Station and landed on Mars approximately nine months later, on the 25th of May 2008, at 68.22 °N latitude, 234.25 °E longitude not far from the edge of the northern polar cap. This spacecraft was the first to successfully land in the Martian polar region. The primary objective of the Phoenix mission was to “follow the water” to verify the presence of subsurface water ice at the landing site and to perform analysis on soil and ice samples from the surface and subsurface to determine the chemistry and mineralogy of the Martian soil. One of the main soil analysis instruments on board Phoenix was the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA). Included in the MECA were four identical Wet Chemical Laboratory (WCL) instruments, Cells 0, 1, 2 and 3 (Figure 1).



Figure 1: Photograph of the Microscopy, Electrochemistry and Conductivity Analyzer (MECA) showing four Wet Chemistry Laboratory (WCL) instruments, Cells 0, 1, 2, and 3 [5]

Each WCL was designed to analyze a solution to which a sample of soil has been added to determine soluble ionic species, pH, and electrical conductivity (EC). While other past missions have used various dry measurement techniques to suggest the geochemistry of Mars, the WCLs were the first instruments to ever perform aqueous analysis on the Martian soil.

This chapter will provide background information about the design of the four WCL instruments, followed by the experimental parameters used for the instrument's pre-flight calibration, characterization and cataloging (C, C, and C) and the results of these experiments. The chapter will conclude with a discussion of the data analysis performed on the soil and the final results from the WCL as to the geochemistry of Mars as it stands to date.

1.2 Background

Each WCL consisted of an actuator assembly and an instrumented beaker assembly. The actuator assembly contained a leaching solution reservoir (which held water plus ionic species for the initial calibration), a 1 cm³ soil sample drawer to receive the soil to be analyzed, a stirrer motor with impeller, a reagent dispenser capable of dispensing five crucibles (a calibration standard, an acid, and three crucibles for sulfate titration), and pressure and temperature sensors. [5]

The instrumented beaker assembly sat directly below the actuator assembly and contained a wide array of sensors (a total of 23 mounted to the four beaker walls) for performing wet chemical analysis on soil samples (Figure 2). Included in the electrode array were: ion selective electrodes (ISEs), pH sensors, a temperature sensor, and electrodes for conductivity, redox potential (ORP), chronopotentiometry (CP), cyclic voltammetry (CV), and anodic stripping voltammetry (ASV). Table 1 lists all 23 sensors inside the WCL beaker



Figure 2: View of sensors on two walls inside of a WCL cell [5]

and their type/composition. For specific details on the fabrication of these electrodes see Kounaves et al. 2009. [5] In addition to the eight flight units (FU) that were designed for spaceflight, which included both beaker and actuator assemblies, six testbeds (TB) were also fabricated. These testbeds consisted of only the beaker assembly containing the same array of sensors as the flight units but with exposed wiring and electronics which allowed for the replacement of faulty electrodes. The testbeds were used for the majority of calibration, characterization and cataloging (C, C, and C). By using the testbeds instead of the flight units it was possible to test a wider variety of potentially damaging conditions without harming the flight qualified units.

1.3 Experimental

Calibration, characterization, and cataloging (C, C, and C) is performed on all new instrumentation prior to use during an actual mission. Calibration is the process of using a series of standards to check the accuracy of the instrument and determine whether or not everything is working properly. During charac-

Table 1: List of the 23 sensors/electrodes inside each WCL [5]

| Sensor/Electrode | Type/Composition |
|---|---|
| Ammonium (NH_4^+) | ISE, PVC membrane doped with Nonactin |
| ASV (heavy metals) | 564 12 μm Au disk microelectrode array (MEA) |
| Barium (Ba^{2+}) | ISE, PVC membrane doped with Ba ionophore-I |
| Bromide (Br^-) | ISE, soils pellet crystal |
| Calcium (Ca^{2+}) | ISE, PVC, membrane doped with ETH-1001 |
| Chloride (Cl^-) | ISE, solid pellet crystal |
| Chloride REF | ISE, solid pellet crystal |
| CP (halides) | 1-mm Ag disk electrode |
| CP (halides) | 1-mm Ag disk electrode |
| CP (redox/acid/base) | 1-mm Pt disk electrode |
| Conductivity | 2-electrode (carbon rings) |
| CV (redox couples) | 0.25 mm Au disk electrode |
| Iodide (I^-) | ISE, solid pettet crystal |
| Lithium 1 REF (Li^+) | ISE, PVC membrane doped with Li ionophore-VI |
| Lithium 2 REF (Li^+) | ISE, PVC membrane doped with Li ionophore-VI |
| Magnesium (Mg^{2+}) | ISE, PVC membrane doped with ETH-7025 |
| Nitrate/perchlorate ($\text{NO}_3^-/\text{ClO}_4^-$) | ISE, PVC membrane doped with ion exchanger |
| ORP (Eh, redox potential) | 1 mm Pt disk electrode |
| pH | Iridium electrode coated with iridium oxide |
| pH 1 | ISE, PVC membrane doped with ETH-2418 |
| pH 2 | ISE, PVC membrane doped with ETH-2418 |
| Potassium (K^+) | ISE, PVC membrane doped with calinomycin |
| Sodium (Na^+) | ISE, PVC membrane doped with Na ionophore-VI |

terization the capabilities and vulnerabilities of the instrument are determined. Finally, cataloging is the process of collecting an instrument response library for comparison to the data collected during the actual mission. This section will outline the experiments performed during calibration and characterization of the WCL testbeds and flight units. Cataloging of WCL was performed on Mars analog soil samples from the McMurdo Dry Valleys (Chapters 2 and 3) and the Atacama Desert (Chapter 4) and will be discussed in the corresponding chapters.

1.3.1 WCL Calibration

Calibration of the WCL sensor array was performed multiple times on the testbeds throughout the C, C, and C process. Calibration of the testbeds was essential to determine whether or not all of the electrodes were operating properly and had not degraded either over time or due to changes in operating conditions, such as changes in temperature or the addition of potentially harmful substances. The flight units were also calibrated several times prior to determining which WCL flight units would be chosen for use aboard Phoenix. Different calibrations were necessary depending on the sensor to be calibrated. Information regarding the calibration of the WCL ISEs and the temperature sensor are discussed in detail.

ISE Calibration: The same five calibration solutions (labelled TS20-TS24) were used to calibrate the ISEs in both the flight units and the testbeds. The concentrations of specific ions of interest were increased from 10^{-5} M to 10^{-2} M. Table 2 lists the concentration of each ion in each test solution

Preparation of Test Solutions: One molar stock solutions of lithium nitrate (LiNO_3), sodium bicarbonate (NaHCO_3), sodium chloride (NaCl),

Table 2: Composition of the test solutions used to calibrate the WCL ISEs

| Ion | TS20 | TS21 | TS22 | TS23 | TS24 |
|-------------------------------|---------|---------|---------|---------|---------|
| | (M) | (M) | (M) | (M) | (M) |
| Li ⁺ | 1.00E-3 | 1.00E-3 | 1.00E-3 | 1.0E-03 | 1.00E-2 |
| Na ⁺ | 1.00E-5 | 3.00E-5 | 1.00E-4 | 1.00E-3 | 1.00E-2 |
| NH ₄ ⁺ | 1.00E-5 | 3.00E-5 | 1.00E-4 | 1.00E-3 | 1.00E-2 |
| K ⁺ | 1.00E-5 | 3.00E-5 | 1.00E-4 | 1.00E-3 | 1.00E-2 |
| Mg ²⁺ | 1.00E-5 | 3.00E-5 | 1.00E-4 | 1.00E-3 | 1.00E-2 |
| Ca ²⁺ | 1.00E-5 | 3.00E-5 | 1.00E-4 | 1.00E-3 | 1.00E-2 |
| Ba ²⁺ | 1.00E-5 | 3.00E-5 | 1.00E-4 | 1.00E-3 | 1.00E-2 |
| NO ₃ ⁻ | 1.03E-3 | 1.09E-3 | 1.30E-3 | 4.00E-3 | 3.10E-2 |
| Cl ⁻ | 5.00E-5 | 1.50E-4 | 6.00E-4 | 6.00E-3 | 6.00E-2 |
| HCO ₃ ⁻ | 1.00E-5 | 1.00E-5 | 1.00E-5 | 1.00E-5 | 1.00E-5 |

ammonium nitrate (NH₄NO₃), potassium chloride (KCl), magnesium nitrate (Mg(NO₃)₂), calcium chloride (CaCl₂), and barium chloride (BaCl₂) were prepared from dried salts (with the exception of Mg(NO₃)₂ which was prepared from the hexahydrate salt). One liter of TS20 was then prepared from the 1 M solutions using the quantities listed in Table 3. Five hundred milliliters of Table 3: Concentration of each 1 M salt solution used to prepare 1L of TS20

| 1 M Solution | Amount Added (μ L) |
|-----------------------------------|-------------------------|
| LiNO ₃ | 1000 |
| NaHCO ₃ | 10 |
| NH ₄ NO ₃ | 10 |
| KCl | 10 |
| Mg(NO ₃) ₂ | 10 |
| CaCl ₂ | 10 |
| BaCl ₂ | 10 |

spike solution (TS20s) was prepared directly from the dried salts (again with the exception of Mg(NO₃)₂ which was prepared from the hexahydrate salt) by adding the quantities listed in Table 4.

Methods of ISE Calibration: Two methods were used for calibration. In the traditional method, five separate test solutions were prepared: TS20,

Table 4: Mass of dried salts used to prepare 500 mL of spike solution (TS20s)

| Salt | Desired Conc. (M) | Amount added (g) |
|---|-------------------|------------------|
| LiNO ₃ | 0.001 | 0.0345 |
| NaCl | 0.1 | 2.922 |
| NH ₄ NO ₃ | 0.1 | 4.002 |
| KCl | 0.1 | 3.7275 |
| Mg(NO ₃) ₂ • 6H ₂ O | 0.1 | 12.821 |
| CaCl ₂ | 0.1 | 5.8549 |
| BaCl ₂ | 0.1 | 10.4116 |

TS21, TS22, TS23, and TS24 (see Table 2 for test solution concentrations). The WCL cell was rinsed three times with 18.2 mΩ water and 25 mL of TS20 was added to the cell. The potential readings were collected for ten minutes. The TS20 solution was then quickly pipetted from the cell and 25 mL of TS21 was added and the new potential readings were collected for five minutes. In turn, the TS22, TS23, and TS24 were then added to the cell and readings were collected for five minutes each.

A variation of this method was later developed to minimize the number of standard solutions prepared and to negate the removal of the test solution in order to increase the concentration. In this spike calibration method, a solution of TS20 was prepared along with a spike solution, TS20s (see Table 4 for concentration of salts in the spike solution). The cell was cleaned three time with 18.2 mΩ of water and 25 mL of TS20 was added to the cell. After collecting the potential for ten minutes, the first spike of TS20s was added raising the concentration of ions to the level present in TS21, and the potential was measured for five minutes. Three more spikes were added, raising the concentration to the levels found in TS22, TS23 and TS24, each time measuring the potential for five minutes. The amount of TS20s added in each spike is listed in Table 5.

In both methods, the concentration of each ion was raised from 10⁻⁵ M to

Table 5: Volume of spike solution (TS20s) added to WCL to sequentially increase the concentration of TS20 to the concentrations of TS21 to TS24

| Solution | TS20s Spike Volume (μL) |
|----------|--------------------------------------|
| TS20 | 0.0 |
| TS21 | 5.0 |
| TS22 | 17.5 |
| TS23 | 227.5 |
| TS24 | 2525.0 |

10^{-2} M. Using specially designed Labview software, graphs of potential versus time were collected. During data processing, the signal from either Lithium REF 1 or Lithium REF 2 was subtracted from the signal for all other ISEs. Figure 3 shows a typical graph of time versus potential (with Lithium REF 2 subtracted) for the calibration of TB4 under ambient laboratory conditions. A calibration curve was then plotted for each ion of interest by plotting the log of the activity of each ion in each test solution (see Table 2 for ion concentrations) versus the average potential response from each spike solution. The corresponding calibrations curves from the calibration run shown in Figure 3 is shown in Figure 4.

Ion Chromatography Analysis of Test Solutions: Table 2 lists the desired molar concentration of each ion in each test solution. However, in the preparation of the five test solutions, incomplete drying of salts, non-exact measuring of salts and uncertainties associated with the balance, glassware, and pipets are all potential sources of error, which deviate the actual concentration of each ion in each test solution from the concentration listed in Table 2. Therefore, a study was performed to determine the average actual concentration with standard deviation of each ion in each test solution by ion chromatography (IC) and compare it to the theoretical concentrations (Table 2). Calibrations were then performed using three different WCL cells, testbeds

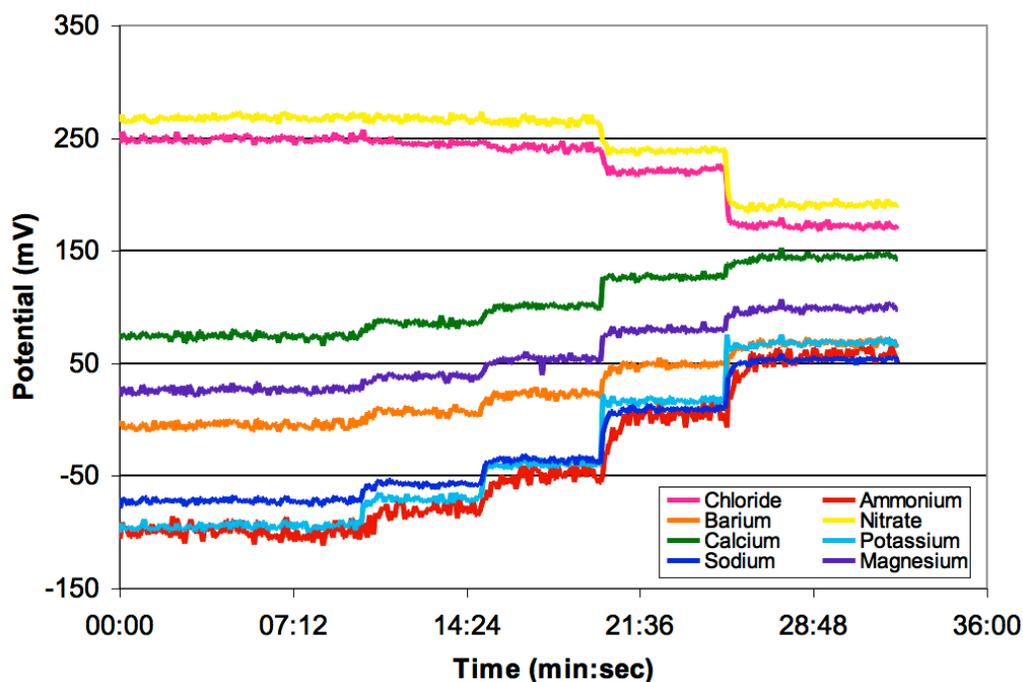


Figure 3: Plot of time (in min:sec) versus ISE potential (in mV) for TB4 during a calibration from TS20 to TS24 under ambient laboratory conditions

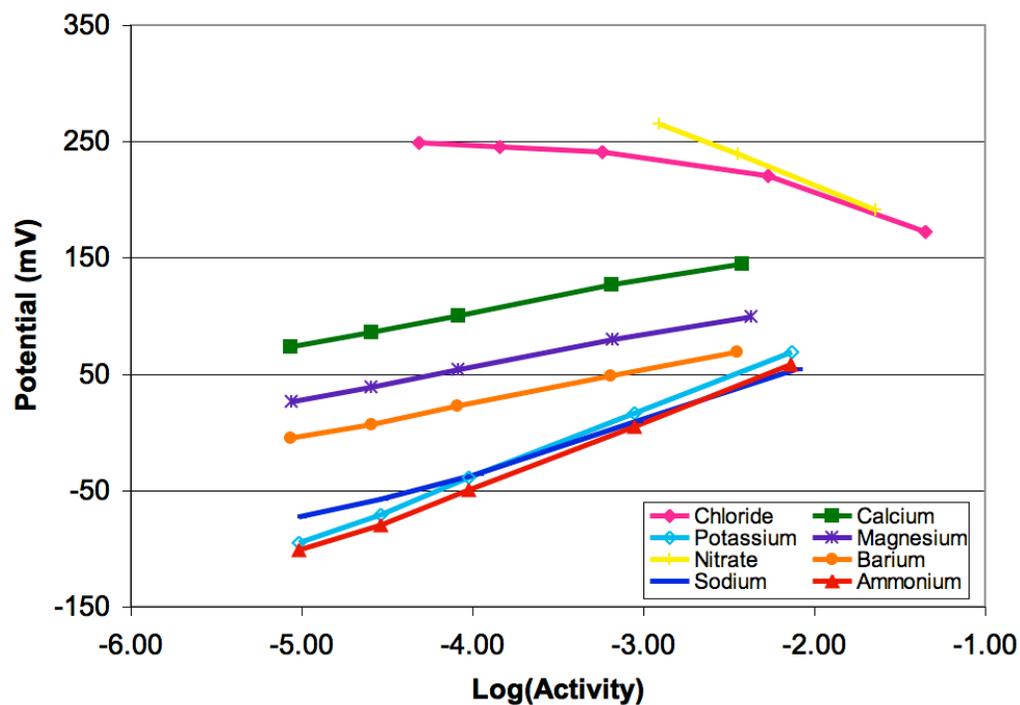


Figure 4: Calibration plot of log(activity) versus ISE potential (in mV) for TB4 for a calibration from TS20 to TS24 under ambient laboratory conditions

2 and 4 (TB2 and TB4) and flight unit 21 (FU21). From the calibrations the solution error, the error in mV response caused by using the theoretical test solution concentrations in place of the actual test solution concentrations, and the instrument error, the standard deviation on the mV response for each ISE, were determined. Comparison of these two types of error could then be made between WCL cells as well as between each other to determine if using the theoretical concentrations over the actual concentrations would affect the calculated slope of the calibration curves.

For this study three batches of test solutions were prepared: Batch 1, Batch 2, and Batch 3. To maximize the potential error in test solution preparation, each batch was prepared by a different individual. All three batches were prepared in the following manner. First, stock solutions of TS20 and TS20s were prepared following the above procedure. Then 25 mL of TS21, TS22 and TS23 were prepared from the stock solution of TS20 by spiking with the corresponding amount of TS20s stock solution listed in Table 5. TS24 was excluded from this study because the concentrations of ions were too high to be run in the IC without dilution, thus introducing additional error.

To calibrate the IC systems for analysis ten IC calibration standards were prepared from commercially available IC stock solutions. Tables 6 and 7 lists the concentration of each cation and anion in each IC standard. Due to the limitations of the IC, it was not possible to calibrate for bicarbonate (HCO_3^-) and thus HCO_3^- was excluded from this study.

Analysis was performed on a pair of Dionex ICS-2000 reagent free ion chromatographic systems (Dionex, Sunnyvale, CA, USA) set-up to run simultaneously. Each system includes a dual-piston pump, high-pressure injection valve with 25 μL sample loop, Dionex DS6 heated conductivity cell and an AS40 automated sampler. For the anions, a Dionex IonPac AS18 analytical

Table 6: IC cation standards for the WCL test solution study

| | Standard 1 | Standard 2 | Standard 3 | Standard 4 | Standard 5 |
|------------------|-------------------|-------------------|-------------------|-------------------|------------|
| Cation | (μM) | (μM) | (μM) | (μM) | (mM) |
| Li^+ | 2.88 | 14.4 | 72.0 | 288 | 1.44 |
| Na^+ | 3.48 | 17.4 | 87.0 | 348 | 1.74 |
| NH_4^+ | 55.4 | 27.7 | 139 | 554 | 2.77 |
| K^+ | 5.12 | 25.6 | 124 | 512 | 2.56 |
| Mg^{2+} | 4.11 | 20.6 | 103 | 411 | 2.06 |
| Ca^{2+} | 4.99 | 25.0 | 125 | 499 | 2.50 |
| Ba^{2+} | 2.91 | 5.83 | 146 | 14.6 | 1.46 |

Table 7: IC anion standards for the WCL test solution study

| | Standard 6 | Standard 7 | Standard 8 | Standard 9 | Standard 10 |
|-----------------|-------------------|-------------------|-------------------|------------|-------------|
| Anion | (μM) | (μM) | (μM) | (mM) | (mM) |
| Cl^- | 28.2 | 14.1 | 56.4 | 1.41 | 7.05 |
| NO_3^- | 0.0 | 0.0 | 80.6 | 1.61 | 4.03 |

column (250 x 4 mm I.D.) and an AG18 guard column (50 x 4 mm I.D.) were used along with an Anion Self-Generating Suppressor 300 (4-mm). The eluent was 23 mM potassium hydroxide with a flow-rate of 1.0 mL/min. For the cations, a Dionex IonPac CS12A analytical column (250 x 4 mm I.D.) and a CG12A guard column (50 x 4 mm I.D.) were used along with a Cation Self-Generating Suppressor 300 (4-mm). The eluent was 20 mM methanesulfonic acid with a flow-rate of 1.0 mL/min.

A sequence was run consisting of the five cation standards (least to most concentrated), the five anion standards (least to most concentrated), and the test solutions from TS20 to TS23 from Batch 1. A blank (18.2 m Ω water) was run at the beginning of the sequence in between the two sets of standards and in between the standards and the test solutions as a quality control measure. The program ran for a total of 32.5 minutes per sample with 30 minutes of analysis and 2.5 minutes for sample injection. The test solutions were run in triplicate with no dilution. Uncertainties associated with the IC analysis

such as the error associated in preparing the calibration standards and the uncertainties of the calibration standards, which ultimately lead to uncertainty in the calibration slopes used to determine the concentration of ions in the test solutions, were not taken into account in this study.

Using the calibration standards, a calibration curve was produced for each ion. The average concentration of each ion with corresponding standard deviation in each of the test solutions in Batch 1 were calculated. A second and third sequence was run following the same parameters discussed above to analyze the test solutions in Batches 2 and 3, respectively. New calibration curves were calibrated for each ion in each sequence and the average concentration of each ion with corresponding standard deviation in each of the test solutions in Batches 2 and 3 were calculated. Finally, an average concentration with standard deviation of each ion on each test solution for all three batches was calculated.

Temperature Sensor Calibration: Each WCL cell contains three separate temperature sensors, one on the drawer, one in the tank holding the leaching solution and one in the beaker. All temperature sensors had a working range of -50 to $+70$ °C (± 0.1 °C). [5] The temperature sensors on the drawer and in the tank were not calibrated at Tufts University because these portions of the WCL were not available. However, the temperature sensor in the beaker of TB3 which was used for all temperature studies was calibrated.

To calibrate the temperature sensor, the test solution, TS20, inside the TB was either cooled or heated to various temperatures from ~ 0 °C to 40 °C. Copper tubing (3 mm O.D. x 1 mm I.D.) was coiled to fit inside the testbed, without touching the sides or bottom, and attached to a refrigerant bath. The refrigerant bath pumped either water (for temperature above 24 °C) or $\sim 70\%$

ethanol in water (for temperatures below 24 °C) through the coil thus heating or cooling the solution to the desired temperature as measured by a digital thermometer, which was also placed inside the cell away from the walls and floor of the cell as well as the coil. The solution was stirred by placing the Orion stirrer inside the copper coil (Figure 5).

The testbed was filled with TS20 solution and the solution was cooled or heated to the desired temperature as measured by the digital thermometer. Once the desired temperature was reached, the potential of the temperature sensor was recorded for ten minutes. The average potential (in mV) was then plotted versus the temperature of the solution (in °C). An example temperature calibration for temperatures cooler than ambient laboratory conditions in TB3 is shown in Figure 6. Temperature calibration was always extremely linear but it was extremely sensitive to all the various wires and internal components of each set-up, and thus if any changes were made to the TB or the rest of the set-up the temperature sensor required recalibration.

1.3.2 WCL Characterization

Initial calibrations of the testbeds and flight units were performed in the laboratory under ambient conditions (24 °C and 1 atm). However, during the actual analysis performed on Mars these are not the conditions under which the sensors were subjected. Therefore it was necessary to characterize the sensors to determine their full capabilities or limitations and to anticipate operation in the Martian environment. All characterization was performed solely on the testbeds, (saving wear and potential damage on the flight units). The effects of ionic strength, pH, temperature and ammonium (NH_3 was a possible contaminant to the soil being a byproduct from the Lander's thruster engines, which could in present generate high levels of NH_4^+ in the WCL cell) were all

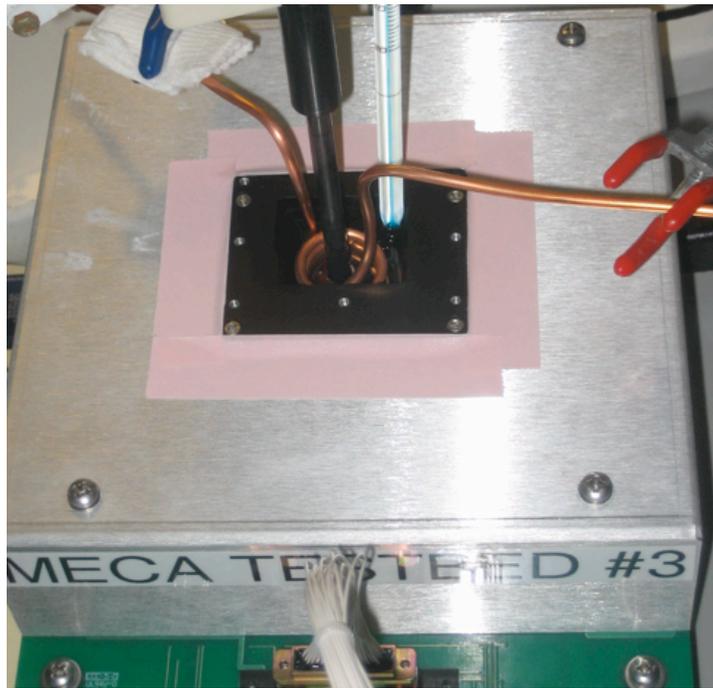


Figure 5: Set-up of Testbed 3 for temperature sensor calibration and subsequent temperature experiments

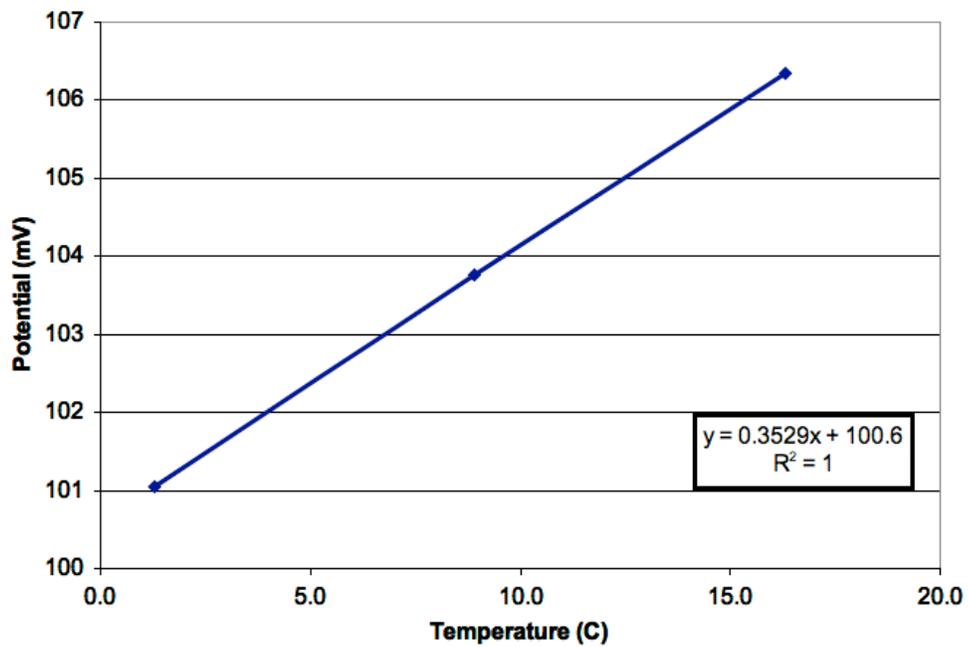


Figure 6: Calibration plot of solution temperature (in °C) versus potential (in mV) for the temperature sensor inside Testbed 3 under colder than ambient laboratory conditions

examined, but only the effects of temperature will be discussed below. The effects of ionic strength, pH and NH_4^+ can be referenced in Kounaves et al. 2009. [5]

Effect of Temperature on Calibration: If only one primary ion is present in solution the response of an ISE can be predicted by the Nernst Equation (Equation 1):

$$E = E_i^\circ + (2.303RT/z_iF)\log(a_i) \quad (1)$$

Where E is the measured potential, E_i° is the standard potential of the electrode for the primary ion i , R is the gas constant, T is the absolute temperature, F is Faradays constant, z is the charge of the primary ion i , and a is the activity of ion i . As seen in Equation 1, it is possible to use the Nernst equation to calculate the effect of temperature on the sensitivity (S) of an ISE. Table 8 lists the theoretical calibration slopes for the -1, +1, and +2 ions at the various temperatures tested.

Table 8: Theoretical ISE sensitivities (in mV) at various temperatures for -1, +1 and +2 ions calculated from the Nernst equation

| Temperature (°C) | S for Z = -1 (mV) | S for Z = +1 (mV) | S for Z = +2 (mV) |
|---------------------|----------------------|----------------------|----------------------|
| 0 | 54.2 | 54.2 | 27.1 |
| 2 | 54.6 | 54.6 | 27.3 |
| 5 | 55.2 | 55.2 | 27.6 |
| 15 | 57.2 | 57.2 | 28.6 |
| 25 | 59.2 | 59.2 | 29.6 |
| 30 | 60.2 | 60.2 | 30.1 |
| 40 | 62.2 | 62.2 | 31.1 |

As seen in Table 8, for a singularly charged ion ($z = 1$) the change in $S = 0.20 \text{ mV}/^\circ\text{C}$ (at 5°C , $S = 55.2 \text{ mV}$ and at 25°C , $S = 59.2 \text{ mV}$), therefore as the temperature decreases there is a slight loss of sensitivity. Even

though the effect of temperature was theoretically calculated for the temperature range to be encountered during operations on Mars, temperature tests were performed in the testbeds to insure that non-Nernstian processes such as restricted diffusion or membrane instability did not add to the difference in sensitivity. To heat or cool the test solutions to the desired temperature, the same heating/cooling system used in the temperature sensor calibration was placed inside the WCL cell, away from the walls and the floor of the cell (Figure 5). Using the same test solutions from the initial calibrations (TS20-TS24) and the spike calibration method, the testbeds were calibrated at 6 different temperatures (2, 5, 15, 24, 30, and 40 °C).

1.3.3 WCL Results

The analytical protocol of WCL experiment on Mars varies greatly from an experiment performed back on Earth in the laboratory. Figure 7 outlines the analytical protocol of a WCL experiment performed on Mars. On the first day of experimentation (Sol A) the leaching solution, equivalent to the TS20 solution used for calibration of the cells on Earth, was thawed in the water tank of the actuator assembly and delivered to the beaker assembly and measured by the sensors for 15 minutes with stirring to provide the first calibration point for the ISEs. A calibrant crucible was then added to the beaker assembly, which contained the salts necessary to bring the solution inside the beaker to the equivalent of the TS21 solution, and provided the second point of the calibration as measured by the ISEs with stirring for 30 minutes. Soil delivered by the robotic arm to the sampling drawer was then added to the beaker and for the remainder of the analysis time on the first Sol (estimated at 200 minutes) the solution was monitored by the ISEs, while stirring, and the voltammetric or potentiometric analyses were performed without stirring. At the end of Sol

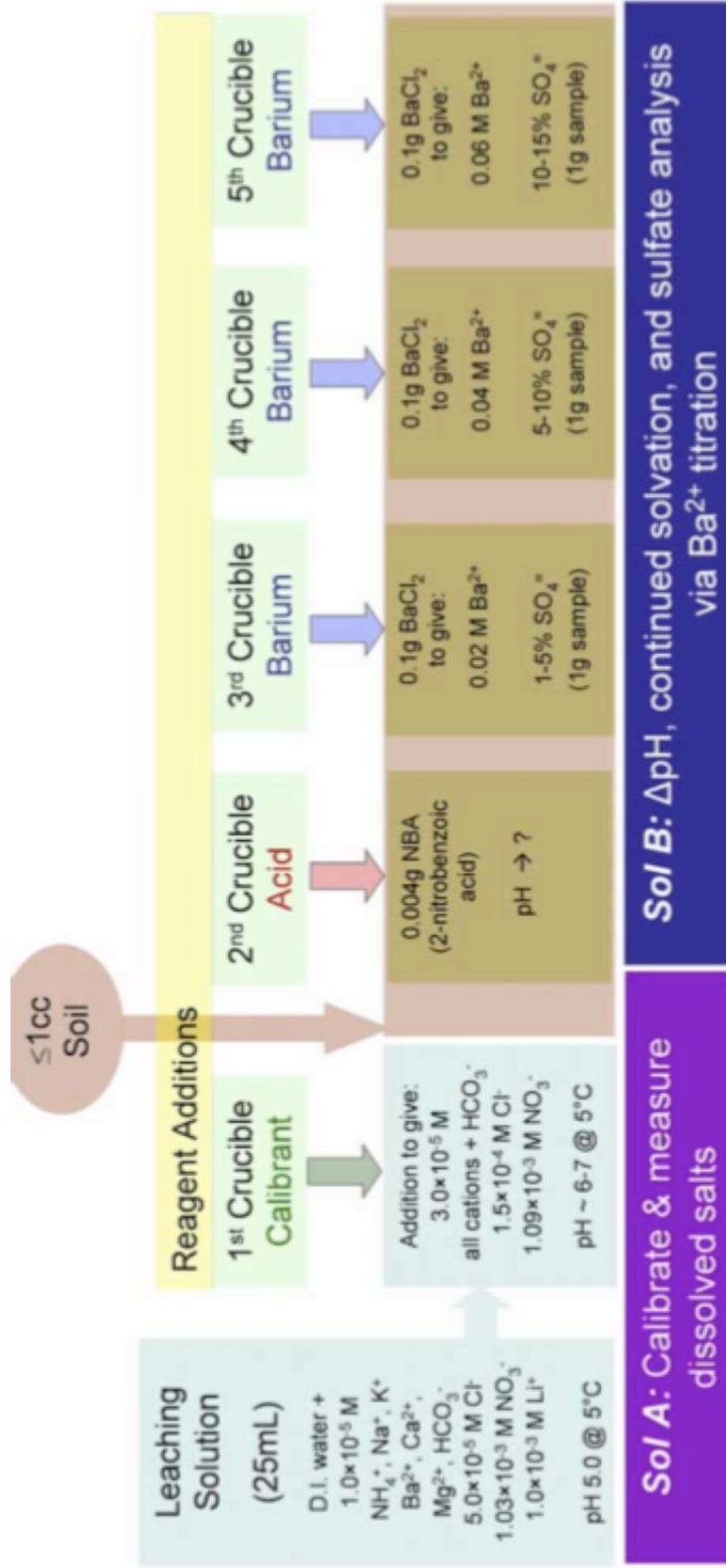


Figure 7: Diagram of WCL analytical protocol performed on Mars [5]

A the WCL was allowed to freeze. [5]

At the start of the second day of analysis (Sol B) the WCL was thawed and the solution was monitored by the sensors for 50 minutes to determine if there were any changes observed after a night of freezing and thawing. A second crucible packed with 0.004 grams of 2-nitrobenoic acid was then added to the beaker to decrease the pH and the solution was monitored for 90 minutes. Finally, one at a time three crucibles containing approximately 0.11 grams of barium chloride were added to the beaker over the course of 45 minutes and the solution was monitored for an additional 90 minutes. [5]

All WCL data returned from the Phoenix spacecraft was in the form of digital numbers. The digital numbers were converted to voltages and currents using parameters determined from preflight calibrations. After conversion the ISE signals were additionally processed to remove systematic fluctuations due to software error. Random noise was also reduced by signal averaging and removal of obvious outliers in the data. Once the signals were cleaned up the ISE voltages were converted to ion activities and concentrations by using the calibrations determined for each sensor preflight and during the WCL analytical protocol. For a detailed description of the data conversion process, see Kounaves et al. 2010. [6, 7]

Determination of the concentration of Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Cl^- shortly after sample addition was fairly straightforward. However, problems arose when trying to determine the concentrations of NO_3^- , Ca^{2+} , and SO_4^{2-} . These sensors did not provide straightforward information as to the amount of ion present and therefore their analysis is discussed in more detail. Although the Cl^- gave a straightforward result shortly after sample addition, as time passed on Sol A the signal continued to decrease, thus the mysterious behavior of this sensor is also discussed.

Nitrate and Calcium ISE Response: The response of the nitrate ISE upon the addition of soil to WCL was a three order of magnitude decrease in signal. Negatively charged ions lower the potential response of an ISE with increasing concentration. This was by far the largest response of any of the sensors to the addition of soil. When the concentration of nitrate was calculated from the change in signal, the amount of nitrate was determined to be equal to several times the mass of sample (~ 1 gram) delivered to the WCL. Therefore, it was impossible the signal was solely the result of the addition of nitrate to the cell. The sensor used for the determination of nitrate was a Hofmeister ISE that will respond to a large number of anionic species. The selectivity of the response is dictated by the Hofmeister series: $\text{ClO}_4^- > \text{I}^- > \text{SCN}^- > \text{ClO}_3^- > \text{CN}^- > \text{Br}^- > \text{S}_2\text{O}_8^{2-} > \text{BO}_3^{3-} > \text{NO}_3^- > \text{HS}^- > \text{HCO}_3^- > \text{Cl}^-$. Any of the anionic species in the Hofmeister series would cause a response of the nitrate sensor in WCL. [6]

Therefore, it was necessary to determine which ion caused the sensor's unusually large response. Several of the ions in the Hofmeister series could be immediately excluded. Those below NO_3^- in the series, HS^- , HCO_3^- , and Cl^- were excluded because they would respond even less selectively than nitrate. Also, it was possible to exclude Br^- and I^- because of the absence of their detection by the halide ISE. The other ions, ClO_4^- , SCN^- , ClO_3^- , CN^- , $\text{S}_2\text{O}_8^{2-}$, and BO_3^{3-} could have possibly caused this response. To test each ion, 3-6 mM was added to a WCL testbed containing TS21 solution and the response of all sensors was monitored to see what ion caused a response most similar to that seen on Mars. [6]

In addition to the unexpected three order of magnitude increase in the Hofmeister series ISE, there was another unexpected response of the calcium ISE. An increase in concentration of calcium should result in a positive increase

in potential, however, when Martian soil was added to the WCL beaker, there was a negative response in potential for the Ca^{2+} ISE. The cause of the decrease in potential of the calcium signal was a suspected interferent which would cause complex formation in the ISE membrane. When testing the possible Hofmeister series ions for the large increase in Hofmeister sensor response, the response of the Ca^{2+} sensor was also monitored to determine if any of those ions also caused a decrease in Ca^{2+} sensor response. If both responses were observed the ion was most likely the mystery ion in the Martian soil. [6]

Chloride ISE Response: The Cl^- ISE also exhibited an interesting response upon the addition of the Martian soil. The proper response of a decrease in mV output upon soil addition was observed indicating an increase of the concentration of Cl^- in solution. However, in both Cell 0 and Cell 2, the mV response did not decrease and level off as was seen for all of the other sensors. Instead there was a consistent decrease in potential of the Cl^- sensor after soil addition (Figure 8). The ISE response was not continuously monitored in any of the WCL cells because the ISEs and stirring were stopped every 30 minutes to perform cyclic voltammetry (CV) scans for 30 minutes. After each CV break the chloride signal decreased indicating more Cl^- was present. In addition, in Cell 2 there was also a continuous increase in conductivity, as measured by the conductivity sensor, after sample addition. Like the ISEs, the conductivity was also not constantly monitored. It was not possible to determine if the conductivity also increased in Cell 0 because the sensor was non-functional. An increase in the conductivity sensor is an indication of an increase in ion concentration. This provided a second indicator that additional Cl^- or some other ion was present in solution.

One hypothesis for this decrease in Cl^- signal is the presence of a chloride

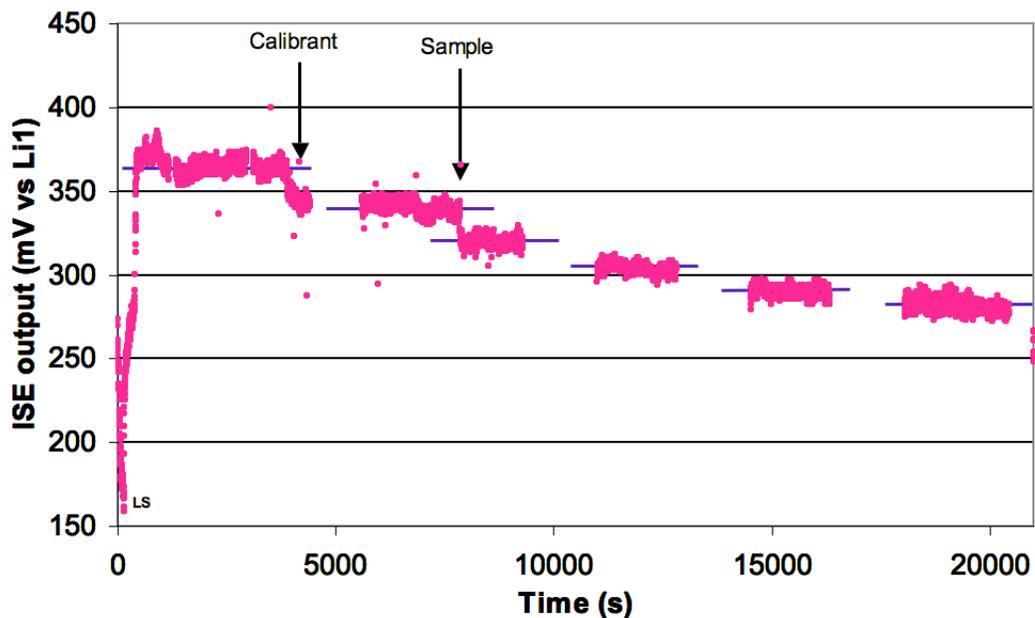
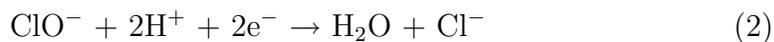


Figure 8: Cl^- ISE response over time for Cell 0 analysis of Rosy Red Sol A. (The breaks in sensor response every 30 minutes are the result of the ISEs being turned off for 30 minutes to perform cyclic voltammetry scans.)

salt in the soil which was sparingly soluble and therefore slowly leaching into solution. However, all chloride are soluble with the exceptions of AgCl , HgCl_2 . Only PbCl_2 is slightly and it is unlikely this salts would be present on Mars. [8]

A second hypothesis to explain these results was irreversible reduction of a chlorate anion, such as hypochlorite (ClO^-), chlorite (ClO_2^-), chlorate (ClO_3^-) or perchlorate (ClO_4^-), to chloride (Cl^-) during the CV scans. Equations 2, 3, 4 and 5 shows the reduction of each chlorate species to chloride.





To test the hypothesis, experiments were performed to mimic the CV scans run on Mars using a solution of 3 mM a given chlorate species in TS21.

As with a typical CV laboratory experiment, a triangular waveform with a constant forward and reverse scan rate was used for the WCL CV experiments. The CV voltages were set between $\pm 1\text{V}$ relative to a Cl^- ISE. The three electrode configuration consisted of a 250 μm diameter Au working electrode, the WCL platinum ORP counter electrode and one of the Cl^- ISE electrodes as a reference. The minimum scan rate which could be achieved was 333 mV/second (due to spacecraft command constraints of CV waveforms to 10 seconds with a maximum of 2015 data points and a minimum potential step of 1 mV). A total of 18 scans were performed per CV measurement (6 gain settings to cover the complete current range and three scan speeds of 333 mV/second and two higher speeds).

Twenty-five milliliters of 3 mM of the chlorate species in TS21 was placed in a beaker with a 2 mm Au working electrode (a smaller 250 μm Au electrode was not available) and a Pt wire counter electrode to perform the CV, and a lab-made Cl^- ISE (calibrated from TS20-TS24) and an Ag/AgCl double-junction reference electrode to measure the Cl^- concentration. Several lab-made Cl^- ISEs were calibrated and the two with the most Nernstian response were used. Several tests were performed with this set-up.

The first test was to determine if ClO_4^- would be reduced to Cl^- after 18 CV scans. The background Cl^- potential was measured with the Cl^- ISE while the solution was stirred. Stirring was stopped and 18 CV scans from $\pm 1\text{V}$ were run at a scan rate of 333 mV/second with a potential step of 1 mV. Stirring was re-started and the Cl^- potential was again measured, waiting enough time for the solution to re-equilibrate. In the second test, the number

of scans was increase for 18 to 36. For the final three tests, instead of running CV scans the voltage was held constant for 1 hour at -1.5 V, -2V and 2V. The mV response of the Cl^- ISE was measured before and after applying the constant voltage to see if under any of these conditions it was possible to reduce ClO_4^- to Cl^- .

In a paper by Horányi and Bakos [9], it was shown that HClO_4 reduction at a platinized electrode led to the production of Cl^- ions in an 8 M HClO_4 solution. There was also mention that the same reduction could possibly occur in the case of smooth Pt electrodes at low ($c \leq 1$ M) HClO_4 concentrations, however, this was not tested. In the WCL cells, two Pt electrodes were present: a 1-mm Pt disk electrode for CP and a 1-mm Pt disk electrode for ORP. Therefore, it was possible that either of these two electrodes could have caused ClO_4^- reduction to Cl^- . Using the same set-up discussed above but exchanging the Au working electrode for a second Pt wire, the experiments were repeated starting with 18 and 36 CV scans at 333 mV/second, followed by 1 hour constant voltage tests from -1 V to as high as -2 V to look for possible reduction of ClO_4^- to Cl^- .

Barium ISE Response - Determination of Sulfate: Sulfur is know to be present on the surface of Mars. The Viking and Mars Rovers (Spirit and Opportunity) both detected the presence of sulfur by x-ray spectrometry. Viking found high concentrations of sulfur 10 to 100 times higher than the sulfur in terrestrial and lunar rock and soil but on the same order of magnitude as the sulfur in Martian meteorites. From the Viking missions the following candidates for sulfur containing compounds on Mars included: Na, Mg, Ca, and Fe sulfates and Fe sulfides. [10]

The Mars rover, Opportunity, also found sulfur in high concentrations,

which was explained as the result of a high abundance of sulfate salts, using multiple types of spectrometers: Mössbauer, miniature thermal emission (Mini-TES) and alpha particle x-ray (APXS). The Mössbauer determined the presence of jarosite ($\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$), a hydroxide sulfate mineral. [11] The Mini-TES indicated the presence of approximately 20 to 40% by wt. Mg and Ca sulfates and approximately 5% jarosite [12], and the APXS revealed sulfur concentrations ranged from 0.52 to 24.7 wt. % SO_3 in various locations. [13]

With all the previous evidence for a sulfur rich Mars and the presence of sulfates through spectrometry, one specific goal of the WCL was to identify the presence of soluble sulfate and determine its concentration through wet chemistry experimentation. The determination of the presence and concentration of sulfate in the Martian soil was not as straightforward as the other ions. Though SO_4^{2-} ISEs were available at the time WCL was being fabricated, there were issues with interferences [14] and limited linear range [15]. Therefore, a different method of sulfate determination was necessary.

Titration of sulfate with barium chloride was selected as the alternative method for sulfate analysis. [16] When Ba^{2+} is added to a solution containing SO_4^{2-} , BaSO_4 will precipitate out of solution. By adding a Ba^{2+} ISE to the WCL cell it was possible to monitor the amount of barium in solution, and subsequently determine the amount of sulfate present. As seen in the WCL analytical protocol (Figure 7), three crucibles each containing a known quantity of BaCl_2 were added one by one to the solution containing the Martian soil sample allowing for the determination of up to 15 wt. % SO_4^{2-} . As long as there were SO_4^{2-} ions in solution, the Ba^{2+} ions would form BaSO_4 and precipitate out of solution, not altering the response of the Ba^{2+} ISE. However, when all of the SO_4^{2-} had formed BaSO_4 , the endpoint of the titration, the additional Ba^{2+} ions would remain in solution and the Ba^{2+} ISE would re-

spond. During the entire titration process Cl^- was also added to the solution, from the BaCl_2 . The total amount of Ba^{2+} added at the endpoint of the titration could therefore be determined from the concentration of Cl^- measured at the point at which the Ba^{2+} signal began to increase. The concentration of Ba^{2+} measured by the Ba^{2+} ISE was subtracted from the known amount of Ba^{2+} added to solution to determine the amount of Ba^{2+} . Since there is a 1:1 ratio of Ba^{2+} to SO_4^{2-} in BaSO_4 (it was known that Ba^{2+} is highly selective to SO_4^{2-} under the analytical conditions on Mars with no interference from CO_3^{2-}), the concentration of Ba^{2+} was equal to the concentration of SO_4^{2-} in solution. [6, 7]

1.4 Results and Discussion

As part of the calibration, characterization, and cataloging (C, C, and C) process, analysis of the test solutions were performed along with calibration of the WCL ISEs and temperature sensors. Additionally, tests were performed to characterize how the temperature affected the WCL calibrations. When the WCL results were received back from Phoenix, the data was processed and analyzed to determine the ions present and their concentration, along with the soil's total conductivity and pH. While some WCL results were fairly straight forward, others involved additional testing back in the lab to verify the WCL findings. This section will present the results of the calibration and characterization, along with a discussion of the Phoenix WCL results. Cataloging results from the Mars analog soils will be discussed in Chapters 2 and 3 for McMurdo Dry Valley soils and Chapter 4 for Atacama Desert soils.

1.4.1 WCL Calibration

A study was performed to determine the average actual concentration with standard deviation of each ion in each test solution by ion chromatography (IC) and compare it to the theoretical concentrations (see Table 2). Calibrations were then performed on three different testbeds/flight units to determine the percent error in the calibration curves when using the theoretical concentrations of the test solutions versus the actual concentrations and compared to the error in the calibration curves between different testbeds/flight units.

The actual concentration of the ions in three batches of test solutions, Batch 1, Batch 2 and Batch 3, with each batch containing test solutions TS20 through TS23 were determined by IC. Table 9 lists the average concentration with standard deviation for each ion (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , NO_3^- , and Cl^-) in each of the four test solutions averaged over all three batches. The standard deviations were small with 80% of the standard deviations $<10\%$ and 97% of the standard deviations $<20\%$. Only one standard deviation was as high as 22%. Comparison of the average actual concentration of the ions in the four test solutions, TS20-TS23 (Table 9) to their theoretical concentrations (Table 2) showed the actual concentrations of most ions were similar to their theoretical values. The ions of Li^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , and NO_3^- were all within a 20% error for all four test solutions. Potassium was within 25% error for all four solutions while Na^+ and NH_4^+ possessed the largest percent errors, with 41% error in TS21 and 228% error in TS20 for Na^+ and 366%, 201%, 139% and 35% error for NH_4^+ in TS20, TS21, TS22 and TS23, respectively.

One potential source of error in the preparation of test solutions was the weighing of the dried salts. Any variation of the mass of the salts added to the TS20 or TS20s solutions would affect the final concentration of ions in solu-

Table 9: Ion concentrations with standard deviation in TS20-TS23 determined by IC analysis

| Ion | TS20 (M) | TS21 (M) | TS22 (M) | TS23 (M) |
|------------------------------|-------------------|-------------------|-------------------|-------------------|
| Li ⁺ | 1.00E-3 ± 2.72E-6 | 1.00E-3 ± 1.18E-5 | 1.01E-3 ± 7.28E-6 | 1.01E-3 ± 7.05E-6 |
| Na ⁺ | 3.27E-5 ± 3.73E-6 | 4.24E-5 ± 1.11E-6 | 1.11E-4 ± 6.27E-6 | 1.03E-3 ± 1.34E-5 |
| NH ₄ ⁺ | 4.66E-5 ± 4.68E-6 | 9.02E-5 ± 2.58E-6 | 2.39E-4 ± 4.46E-6 | 1.34E-3 ± 1.73E-5 |
| K ⁺ | 1.22E-5 ± 2.22E-6 | 3.15E-5 ± 3.83E-6 | 1.03E-4 ± 1.76E-6 | 1.03E-3 ± 7.79E-6 |
| Mg ²⁺ | 8.30E-6 ± 6.08E-7 | 2.91E-5 ± 1.82E-6 | 1.03E-4 ± 1.46E-6 | 1.06E-3 ± 1.14E-5 |
| Ca ²⁺ | 9.68E-6 ± 7.76E-7 | 2.88E-5 ± 1.99E-6 | 9.76E-5 ± 2.85E-6 | 1.00E-3 ± 1.15E-5 |
| Ba ²⁺ | 8.11E-6 ± 1.54E-6 | 2.94E-5 ± 2.80E-6 | 1.00E-4 ± 5.08E-6 | 1.03E-3 ± 2.25E-4 |
| NO ₃ ⁻ | 1.09E-3 ± 3.38E-8 | 1.15E-3 ± 4.97E-8 | 1.30E-3 ± 1.28E-7 | 4.30E-3 ± 1.38E-7 |
| Cl ⁻ | 4.92E-5 ± 5.75E-6 | 1.70E-4 ± 7.39E-6 | 5.85E-4 ± 7.12E-5 | 6.41E-3 ± 2.11E-4 |

tion. When the concentration of each ion in each test solution was calculated from the mass of salts added to solution most of the final concentrations of ions were identical, however, the concentration of some ions changed slightly. Comparison of the concentration of each ion in each test solution as calculated from the mass of salts added to solution to the concentration range determined via IC analysis did not change the overall results discussed above.

Calibrations were performed on three different WCL cells: Testbed 2 (TB2), Testbed 4 (TB4) and Flight Unit 21 (FU21) using TS20 through TS23. For TB2, the average potential (in mV) at each point in the calibration (TS20, TS21, TS22 and TS23) were recorded and used along with the theoretical concentration of each ion in each test solution (Table 2) to produce calibration curves for each ion. Then the average actual concentration of each ion in each test solution (Table 9) was used to determine the new potential (in mV) at each point of the calibration. The difference between the two mV readings for each ion at each point of the calibration curve were recorded. This process was repeated three times and the results were averaged. The error in potential for each point of the calibration curve for each ion caused by using the theoretical ion concentrations instead of the actual ion concentrations is the solution error. The solution error was then compared to the instrument error for each ion at each point in the calibration. To determine the instrument error, the standard deviation of each mV reading for each ion at each point of the calibration curve (TS20, TS21, TS22, and TS23) was determined. This process was also repeated three times and the results were averaged. The average solution error and average instrument error (at calibration points TS20, TS21, TS22, and TS23) were then determined for the other two WCL cells, TB4 and FU21. The results for all three WCL cells were similar so the solution error and instrument error for all three WCL cells were averaged.

The ratio of solution error to instrument error for the combined three WCL cells: TB2, TB4 and FU21 was then determined. When the ratio of solution error to instrument error was $>1:1$, the error caused by using the theoretical test solution concentration was greater than the ISE noise of the ISE and would affect the slope of the calibration, but when the ratio of the solution error to instrument error was $\leq 1:1$, the error caused by using the theoretical test solution concentration would not affect the slope of the calibration because it would be within the noise of the ISE. Table 10 lists the ratio of solution to instrument error for each of the ions in each of the four test solutions averaged over the three WCL cells. The ions K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , and NO_3^-

Table 10: Ratio of the solution error, caused by using the theoretical test solution values instead of the actual test solution values, to the instrument error caused by the standard deviation of the ISEs in the WCL cells, averaged over three WCL cells: TB2, TB4 and FU21. A range of ratios is given to show the 68% confidence interval

| | TS20 | TS21 | TS22 | TS23 |
|-----------|------------|------------|------------|-----------|
| Ion | (ratio) | (ratio) | (ratio) | (ratio) |
| Na^+ | 5.5-11.6:1 | 2.7-4.7:1 | 1.6-3.9:1 | 0.3-0.7:1 |
| NH_4^+ | 5.3-19.4:1 | 4.7-12.7:1 | 3.3-10.7:1 | 1.1-3.2:1 |
| K^+ | 0.4-4.7:1 | 0.3-1.5:1 | 0.1-0.8:1 | 0.2-0.7:1 |
| Mg^{2+} | 0.2-3.4:1 | 0.3-1.0:1 | 0.1-0.4:1 | 0.2-0.6:1 |
| Ca^{2+} | 0.1-1.3:1 | 0.02-0.7:1 | 0.1-0.7:1 | 0.5-1.1:1 |
| Ba^{2+} | 0.7-3.0:1 | 0.01-0.9:1 | 0.1-0.6:1 | 0.1-0.4:1 |
| NO_3^- | 0.4-3.0:1 | 0.05-1.6:1 | 0.7-2.4:1 | 0.5-2.4:1 |
| Cl^- | 0.4-8.1:1 | 0.04-3.1:1 | 0.4-2.9:1 | 0.5-5.9:1 |

gave a ratio of $\leq 1:1$ for all four test solutions, within a 68% confidence interval (or one standard deviation). This study showed that for the majority of the ions in the WCL cells the theoretical concentration of each ion in TS20-TS23 could be used for calibration of the WCL cells without affecting the slope value by more than the standard deviation of the ISE response. However, this was not the case for Na^+ in TS20-TS22 or NH_4^+ in TS20-TS23. For these ions, using the theoretical concentration of these ions would affect the the slope

value by more than the standard deviation of the ISE response.

It must be restated that the three test solution batches were prepared by three different individuals at three separate times to produce a worst case scenario. Therefore, having only two ions which exhibit a $>1:1$ solution error to instrument error, is a fairly good result. This study shows the importance of careful preparation of the WCL test solutions, especially from batch to batch, and the possible negative affect of poor solution preparation on the calibration of the WCL cells.

1.4.2 WCL Characterization

Effect of Temperature on Calibration: The effect of temperature on calibration was studied by calibrating TB3 at various temperatures ranging from 2°C to 40°C . As seen in Table 11, there was little change in the sensitivity of the ISEs over this temperature range. The experimental values for the sensitivities did not exactly match the calculated theoretical values in Table 8. In the theoretical calculation a singularly charged ion ($Z = 1$) had a change in $S = 0.20 \text{ mV}/^{\circ}\text{C}$ while in this study the change in $S = 0.03$ to $0.22 \text{ mV}/^{\circ}\text{C}$ when measuring the change from 5°C to 24°C . However, the general trend of decreasing sensitivity with decreasing temperature was observed and therefore all ISE electrodes performed as expected at the temperatures encountered during operations on Mars.

1.4.3 WCL Results

During the course of the 152 sol mission (1 sol = ~ 24.5 Earth hours [17]), the robotic arm on the Lander delivered soil to all four of the WCL cells, Cell 0, Cell 1, Cell 2 and Cell 3, from four different locations on the Martian surface: Rosy Red, Sorceress 1, Sorceress 2, and Golden Goose, respectively. Three of

Table 11: Experimental ISE sensitivities at various temperatures (Testbed 3)

| Temperature (°C) | Na ⁺ (mV) | NH ₄ ⁺ (mV) | K ⁺ (mV) | Mg ²⁺ (mV) | Ca ²⁺ (mV) | Ba ²⁺ (mV) | Cl ⁻ (mV) | NO ₃ ⁻ (mV) |
|---------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|
| 2 | 42.53 | 51.89 | 50.25 | 22.00 | 23.02 | 25.84 | -46.92 | -55.54 |
| 5 | 43.85 | 56.18 | 53.48 | 24.70 | 23.5 | 27.01 | -48.44 | -57.10 |
| 15 | 43.98 | 54.77 | 55.09 | 24.91 | 26.57 | 27.75 | -49.41 | -59.09 |
| 24 | 44.44 | 57.09 | 57.35 | 27.79 | 28.92 | 29.13 | -52.61 | -58.48 |
| 30 | 43.49 | 59.79 | 62.34 | 26.70 | 27.96 | 27.08 | -55.20 | -60.92 |
| 40 | 44.51 | 63.78 | 63.98 | 29.84 | 29.49 | 30.78 | -55.94 | -66.97 |

the four cells, Cell 0, Cell 1 and Cell 2 showed successful transfer of the soil into the cell while the fourth, Cell 3, showed no indication that any soil reached the cell. This turned out to be advantageous because it allowed for Cell 3 to be used as a blank. [6, 7] The WCL instruments were operated a total of 21 times during the surface science phase of the mission and returned several different types of data including: (1) ISE potentials, (2) solution electrical conductivity, (3) pressure, (4) temperature, (5) redox potential, (6) voltammetry, and (7) chronopotentiometry. Only the results of ISE potentials, pH, and solution electrical conductivity will be discussed herein as the analysis and results of voltammetry and chronopotentiometry are still under investigation.² [6, 7]

ISE Results: Using the preflight calibrations along with the data from the two calibration points collected during WCL analysis, the ion concentration of Na⁺, NH₄⁺, K⁺, Mg²⁺, and Cl⁻ in solution shortly after addition of Martian soil were determined. Table 12 lists the measured concentration of each ion to leach from 1 cm³ of Martian soil with an assumed density of 1g/cm³, into 25 mL of pure water determined by each of the three WCL cells. The error in concentration measurements is reported at ±20% for +1 and -1 ions and ±50% for +2 ions. An average is also reported for Cells 0 and 2. Cell 1 was

²Recently the redox potential (E_h) was determined for the Phoenix WCL Rosy Red sample soil solution: $E_h = 253 \pm 6$ mV a pH of 7.7 ± 0.1 . [18]

Table 12: Ion concentrations of Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Cl^- in solution (in mM) calculated from the WCL ISE responses when 1 cm^3 of the Phoenix Mars Soil (with an assumed density of 1 g/cm^3) was added into 25 mL of TS21 solution. The background concentration of TS21 was subsequently subtracted to determine the concentration of each ion if dissolved in 25 mL of pure water. The error in concentration is reported as $\pm 20\%$ for +1 and -1 ions and $\pm 50\%$ for +2 ions. Adapted from [6, 19]

| | Rosy Red | Sorceress 1 | Sorceress 2 | |
|-----------------------|--------------|--------------|--------------|-----------------|
| Ion | Cell 0 | Cell 1 | Cell 2 | Average |
| Na^+ (mM) | 1.4 | 1.10 | 1.4 | 1.4 ± 0.3 |
| K^+ (mM) | 0.36 | 0.17 | 0.39 | 0.39 ± 0.08 |
| NH_4^+ (mM) | Not Detected | Not Detected | Not Detected | Not Detected |
| Mg^{2+} (mM) | 2.9 | 2.20 | 3.7 | 3.3 ± 1.7 |
| Cl^- (mM) | 0.6 | 0.24 | 0.47 | 0.47 ± 0.09 |

excluded from the average because it appeared to receive a sample volume of soil 25-35% smaller than the amount delivered to Cells 0 and 2. [19]

For the other ions, Ca^{2+} , NO_3^- , and SO_4^{2-} , data analysis was not as straight forward. Determination of the concentration of these ions that leached from 1 cm^3 of Martian soil, with an assumed density of 1 g/cm^3 , into 25 mL of pure water warrants further discussion. The determination as to why there was a decreasing potential signal for the Cl^- sensor after sample addition is also discussed.

Nitrate and Calcium ISE Response: Analysis of several anions in the Hofmeister series was performed to determine a plausible ion which would provide the three order of magnitude decrease in signal potential seen in the WCL cells for the “nitrate” ISE as well as affect the Ca^{2+} ISE by causing the sensor to exhibit a negative response. Of the ions tested (ClO_4^- , SCN^- , ClO_3^- , CN^- , BO_3^{3-} , and $\text{S}_2\text{O}_8^{2-}$) only perchlorate gave the desired responses for both the Hofmeister and Ca^{2+} ISEs. While the possibility exists that another chemical species could be present on Mars that would also cause these

same results, it is highly unlikely. [6]

Re-calibration of a WCL flight unit that was not used on the spacecraft allowed for calibration of the Hofmeister (perchlorate) sensor. By using the calibration it was possible to determine the concentration of ClO_4^- leached from one gram of Martian soil with an assumed density of $1\text{g}/\text{cm}^3$ into 25 mL of pure water in each WCL cell (Table 13). The average perchlorate concentration

Table 13: Ion concentrations of Ca^{2+} and ClO_4^- in solution (in mM) calculated from the WCL ISE responses when 1 cm^3 of the Phoenix Mars Soil (with an assumed density of $1\text{ g}/\text{cm}^3$) was added into 25 mL of TS21 solution. The background concentration of TS21 was subsequently subtracted to determine the concentration of each ion if dissolved in 25 mL of pure water. The error in concentration is reported as $\pm 20\%$ for ClO_4^- and $\pm 50\%$ for Ca^{2+} . Adapted from [19]

| | Rosy Red | Sorceress 1 | Sorceress 2 | |
|-----------------------|----------|-------------|-------------|----------------|
| Ion | Cell 0 | Cell 1 | Cell 2 | Average |
| ClO_4^- (mM) | 2.6 | 2.10 | 2.2 | 2.4 ± 0.5 |
| Ca^{2+} (mM) | 0.55 | 0.42 | 0.6 | 0.60 ± 0.3 |

was calculated as $2.4\text{ mM} \pm 0.5\text{ mM}$ which is equivalent to 0.6 wt. % in the soil, a significant contribution to the the soil sample. [6, 19]

It was previously known that ClO_4^- interferes with the Ca^{2+} ISE causing a Nerstian decrease of -29 mV for every half decade increase in the concentration of perchlorate. [20] By re-calibrating the Ca^{2+} sensor in one of the WCL flight units that was not used on the spacecraft in the presence of perchlorate it was possible to determine the concentration of calcium leached from 1 cm^3 of Martian soil with an assumed density of $1\text{g}/\text{cm}^3$ into 25 mL of pure water in each WCL cell on Mars (see Table 13). The average calcium concentration present in the Martian soil was $0.60\text{ mM} \pm 0.3\text{ mM}$. [6, 19]

Due to the nature of the Hofmeister series ISE and its high selectivity for perchlorate over nitrate it was not possible to determine the presence or absence of nitrate in the Martian soil. The inability of the WCL to analyze for

nitrate in the soil means there is still no direct analysis of nitrate in Martian soil. However, there is some evidence of the possibility of nitrates on Mars.

The Viking mission determined there was approximately 0.2 mbar of N_2 in the Martian atmosphere. However, it has been estimated that early Mars had an atmosphere with anywhere from 3 to 300 mbar of N_2 . There are two possibilities as to the fate of the nitrogen: (1) the N_2 gas could have escaped into space and (2) the N_2 gas could have been converted to NH_4^+ attached to clays and/or NO_2^- and NO_3^- and buried in the soil. Figure 9, depicts the proposed major pathways of the nitrogen cycle on early Mars.

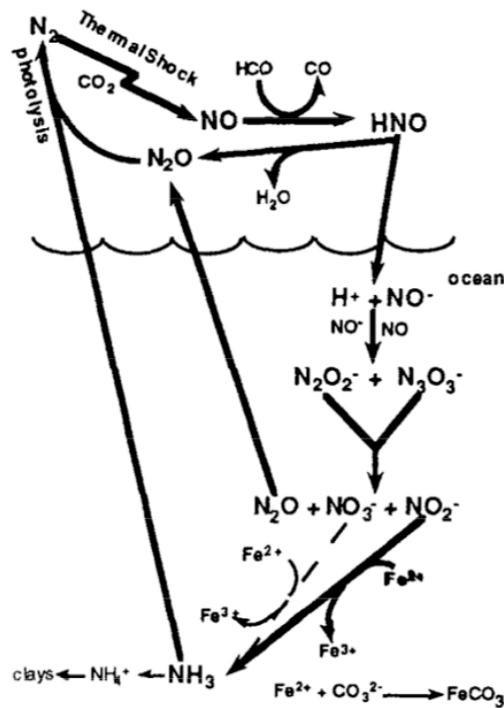


Figure 9: Proposed major pathways of the nitrogen cycle on early Mars [21]

As seen in Figure 9, for the conversion of N_2 to NO_2^- and NO_3^- it would require the presence of liquid water on the surface of Mars for an extended period of time in Mars' early history. In the absence of water the NO_2^- and NO_3^- would accumulate in the Martian soil. [21] The accumulation of nitrates

and its stability in a highly arid and mostly biologically inactive environment, similar to Mars, has been seen on Earth in the Antarctic [22] and the Atacama Desert. [23, 24, 25]

The missing N_2 from the Martian atmosphere from its early history to the present day suggests the possibility of nitrate in the Martian soil. Likewise, nitrates have also been detected in low abundances in both the EETA79001 and Nakhla meteorites. The analysis of these meteorites via FTIR showed the presence of features at 1375 cm^{-1} and 1630 cm^{-1} which are consistent with nitrate. The origin of the nitrate found in these meteorites is unclear. Isotopic nitrogen analysis of the nitrate in the meteorites differs greatly from the nitrogen isotopes in the present day Martian atmosphere. [26] At the present time, the only way to determine for certain whether nitrate is in fact present in the Martian soil will be by analysis during a future mission.

Chloride ISE Response: The hypothesis that the continual decrease in mV response of the Cl^- ISE was due to the reduction of a chlorate anion to chloride was strengthened with the discovery that the “nitrate” ISE was actually measuring a chlorate species, perchlorate, in the Martian soil leachate solution. This hypothesis was therefore tested using a solution of $3\text{ mM } ClO_4^-$ in TS21 to see if the perchlorate could be reduced to chloride (see Equation 5) during the cyclic voltammetry (CV) scans. There was no noticeable decrease in mV response for the Hofmeister ISE measuring the concentration of perchlorate. However, it was possible the change may not have been noticeable due to the high concentration of perchlorate present in solution (0.6 wt. %).

After performing both 18 and 36 CV scans using an Au working electrode and Pt counter electrode, there was no change in Cl^- ISE mV response indicating no measurable amount of ClO_4^- was reduced to Cl^- . It was therefore

unlikely perchlorate would have been reduced to chloride under the conditions of the CV experiment performed on Mars. Additional tests at three constant voltages also resulted in no Cl^- ISE response. Thus, perchlorate reduction to Cl^- by reduction with the Au and Pt electrodes used in the WCL CV experiments was ruled out as the cause of the increase in $[\text{Cl}^-]$ seen in the WCL data. When the working electrode was switched to a second Pt wire and the tests were repeated, the result was the same, no significant change in potential for the Cl^- ISE. Therefore, the two Pt electrodes in the WCL were also ruled out as being capable of reducing ClO_4^- to Cl^- .

It was determined from all of the above experimentation the increase in the Cl^- signal was not the result of the electrochemical reduction of ClO_4^- . In analyzing the data collected from Cell 3 (the “blank” run) it was clearly evident that both the Cl^- and the Ba^{2+} ISEs showed increased concentration after the drawer was opened for sample addition even though no sample was added to the solution. This result was most consistent with accidental addition of BaCl_2 from one or more of the three BaCl_2 crucibles designed to measure SO_4^{2-} . It is believed BaCl_2 contamination was the most likely cause of the Cl^- increase seen in Cells 0 and 2 as well as the cause of the increase in conductivity seen in Cell 2.

Barium Response - Determination of Sulfate: Determination of the soluble sulfate present in the Martian soil was to be detected by BaCl_2 titration, precipitating SO_4^{2-} as BaSO_4 and monitoring the Ba^{2+} concentration to indirectly determine the SO_4^{2-} concentration. The three BaCl_2 containing crucibles were supposed to be released at specific time intervals, however, when monitoring the Cl^- ISE response after soil sample addition the concentration of Cl^- was slowly and steadily increasing with time at a rate of

approximately 1.5 mM/L/hour. This increase in Cl^- concentration was attributed to the BaCl_2 leaching from the crucibles into the cell over the course of Sol A. Though the titration did not occur exactly according to plan it was still possible to use the titration curves from Cell 0 and Cell 2 (the Ba^{2+} sensor in Cell 1 was non-functioning) to determine the total concentration of soluble sulfate, $[\text{SO}_4^{2-}]_T$, via the following equation (Equation 6):

$$[\text{SO}_4^{2-}]_T = \Delta[\text{Cl}^-]/2 \quad (6)$$

where the change in Cl^- concentration, $\Delta[\text{Cl}^-]$, was measured from immediately after soil sample addition to the start of the increase in Ba^{2+} signal from the Ba^{2+} ISE.

Table 14 lists the $[\text{SO}_4^{2-}]_T$ leached from one gram of Martian soil with an assumed density of $1\text{g}/\text{cm}^3$ into 25 mL of pure water in each WCL cell. The

Table 14: Ion concentrations of SO_4^{2-} in solution (in mM) calculated from the response of the Ba^{2+} and Cl^- WCL ISEs when 1 cm^3 of the Phoenix Mars Soil (with an assumed density of $1\text{ g}/\text{cm}^3$) was added into 25 mL of TS21 solution. The error in concentration is reported as $\pm 50\%$. Adapted from [7]

| | Rosy Red | Sorceress 1 | Sorceress 2 | |
|-------------------------|----------|----------------|-------------|----------------|
| Ion | Cell 0 | Cell 1 | Cell 2 | Average |
| SO_4^{2-} (mM) | 4.8 | Not Determined | 5.9 | 5.4 ± 0.78 |

average was determined to be 1.1 ± 0.5 wt. % sulfur reported as SO_3 in the soil. [7] This result was much lower than expected based on the finding from the Mars rover, Opportunity, which found concentrations ranging from 0.52 to 24.7 wt. % as SO_3 . This could indicate either there was much less sulfate present in the north polar regions of Mars than closer to the equator near Meridiani Planum where the Opportunity landed or the sulfur/sulfate was in a less soluble or insoluble form.

pH: Three different pH sensors were present inside each WCL cell, two H⁺ ISEs and an iridium electrode coated with iridium oxide (see Table 1). The sensors were all calibrated preflight using standard buffer pH solutions. As with the ISEs, it was necessary to have at least one stable and accurate calibration point determined on Mars prior to sample addition. However, determination of this point was not entirely straightforward due to the partial pressure of CO₂ (P_{CO_2}) which must be known for the WCL beaker and tank headspace prior to calibration. Therefore, the calibration point was taken after the leaching solution was added but before the WCL beaker was exposed to the Martian atmosphere. At this time the WCL cell was at CO₂ equilibrium and thus the P_{CO_2} was known. [6]

Of the nine pH sensors present in the three WCL cells which received soil (Cells 0-2) only three sensors were considered reliable. The other six sensors were considered unreliable due to either high noise levels or large drifts which prevented a reliable calibration point to be determined. The three working pH sensors were pH 1 in Cell 1, pH 1 in Cell 2 and pH 2 in Cell 2. The average pH of the soil when leached in 25 mL of TS21 was determined as 7.7 ± 0.3 . [6] When the 4-nitrobenzoic acid was added to solution, the pH did not change. Therefore, not only was the soil determined to be slightly alkaline in pH but also pH buffering at ≥ 1 mM. [19] Calcium carbonate has been suggested as the most likely candidate for the buffering because 3-5% calcite (CaCO₃) was detected in the soil by another instrument aboard Phoenix, the Thermal and Evolved Gas Analyzer (TEGA). [27]

The pH measurements by WCL were the first ever wet chemistry pH measurements to be taken of the Martian soil. Prior to the WCL measurements the only information on the acid-base chemistry of Mars was indirect and deduced from the Viking biology experiment. This indirect method concluded the soil

on Mars was weakly to highly acidic due to the accumulation of dry acids. [28] Subsequently, the Mars Exploration Rovers (MER) found high concentrations of sulfur-containing minerals on the Martian surface, including jarosite which forms in a strongly acidic environment. This added to the theory of an acidic Mars. [11] Thus the discovery of a moderate soil pH by direct measurement of the Martian soil by WCL was in some ways a surprise. However, the Viking and MER missions landed much closer to the equator and found much higher sulfur/sulfate compounds than were determined by Phoenix. Therefore, the pH directly determined at one location in the north polar region of Mars may not be representative of the entire planet, and the pH of the soil could still be acidic closer to the equator. Direct pH measurements need to be taken at a variety of locations on the planet before it can be said whether Mars as a planet is acidic, basic or neutral.

Solution Electrical Conductivity: Solution electrical conductivity was also successfully measured by a two carbon ring conductivity sensor (see Table 1) in two of the WCL cells (Cells 1 and 2). The conductivity sensor in Cell 0 was extremely noisy. To convert the conductance (in μS) to solution electrical conductivity (in $\mu\text{S}/\text{cm}$), a cell constant was used which was determined pre-flight during the calibration process. Since conductivity is affected by temperature with a 2% increase per 1°C , the specific conductivity was corrected to 25°C to determine the total solution conductivity. [6]

The total solution conductivity measured $1370 \mu\text{S}/\text{cm}$ in Cell 1 and $1900 \mu\text{S}/\text{cm}$ in Cell 2. Both values have significant uncertainties which are attributed to: (1) the conductance of the leaching solution pre-flight ($82 \mu\text{S}$) differing from the conductance of the leaching solution on Mars ($102 \mu\text{S}$ in Cell 1 and $116 \mu\text{S}$ in Cell 2) and (2) different cell constant values for each cell

calculated pre-flight (1.51 cm^{-1} for Cell 1 and 1.61 cm^{-1} for Cell 2). [6] The measured conductivity of each cell, which acquired a soil sample (Cells 0-2), was lower than the conductivity as measured by the conductivity sensor in that cells, with an average value of $866 \mu\text{S}/\text{cm}$. The conductivity calculated from the ions in solutions as measured by the ISEs (with an average value of $866 \mu\text{S}/\text{cm}$) was approximately one-half of the conductivity as measured by the conductivity sensors indicating there were ionic species present in the cells not determined by the ISEs and the concentration of the unmeasured ionic species was lower or comparable to the concentration on the ions measured. It has been suggested carbonate and/or bicarbonate were responsible for most of this discrepancy, because while it was not possible for WCL to detect these species, TEGA was able to detect 3-5% calcium carbonate in the soil. [27]

1.4.4 Geochemist's Workbench [®] Modeling of Martian Soil

The WCL instruments aboard the 2007 Phoenix Mars mission were the first instruments to perform wet chemistry on soil from the surface of Mars. Using an array of ISEs, and other sensors the concentration of a variety of soluble ions to leach from 1 cm^3 of soil with an assumed mass of 1 gram into 25 mL of pure water was detected (Table 15) along with soil's pH (7.7 ± 0.3) and total solution conductivity ($1635 \mu\text{S}/\text{cm} \pm 375 \mu\text{S}/\text{cm}$ at $25 \text{ }^\circ\text{C}$). The results from Table 15 indicate a soil dominated by soluble ClO_4^- , SO_4^{2-} , Mg^{2+} , and Na^+ with contributions of K^+ , Ca^{2+} and Cl^- . Due to the high levels of ClO_4^- dominating the signal from the Hofmeister ISE it was not possible to discern the presence or absence of NO_3^- . Likewise, conductivity measurements indicate there were additional unmeasured ions present in solution, most likely carbonate or bicarbonate, due to the solution's pH and TEGA's analysis of 3-5% calcite (CaCO_3) in the soil. [6, 19, 7]

Table 15: Ion concentrations of Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , and ClO_4^- in solution (in mM) calculated from the WCL ISE responses when 1 cm^3 of the Phoenix Mars Soil (with an assumed density of 1 g/cm^3) was added into 25 mL of TS21 solution. The background concentration of TS21 was subsequently subtracted to determine the concentration of each ion if dissolved in 25 mL of pure water. The error in concentration is reported as $\pm 20\%$ for +1 and -1 ions and $\pm 50\%$ for +2 ions. (Compilation of Tables 12, 13 and 14) [7]

| Ion | Concentration in Solution (mM) |
|--------------------|--------------------------------|
| Na^+ | 1.4 ± 0.3 |
| K^+ | 0.39 ± 0.08 |
| NH_4^+ | Not Detected |
| Mg^{2+} | 3.3 ± 1.7 |
| Ca^{2+} | 0.6 ± 0.3 |
| Cl^- | 0.47 ± 0.09 |
| ClO_4^- | 2.4 ± 0.5 |
| SO_4^{2-} | 5.4 ± 0.78 |

The WCL ISEs did not necessarily measure the ionic concentration of all of the species at equilibrium but rather gave a snapshot of ionic composition at the time directly after soil addition to the cell. Therefore, *Geochemist's Workbench*® (GWB) was used to perform equilibrium calculations on the Mars WCL results. The solution pH, total conductivity and ion concentrations measured by WCL were constrained under the Martian conditions of 7°C and 4 mbar CO_2 to determine the concentration of species most likely to be present in solution at equilibrium after adding one gram of Martian soil to 25 mL of pure water. GWB was also used to determine the most likely minerals and species present in the Martian soil which could have given the measured/calculated ionic concentrations seen by the WCL ISEs. Table 16 shows the best GWB model to date. [7]

1.5 Conclusions

The results from the WCL experiments have greatly added to the understanding of the chemistry and habitability of Mars. It was believed from the results

Table 16: Concentration of species likely present in solution after adding 1 cm³ of Phoenix Mars Soil into 25 mL of pure water and the amounts of the minerals or species required in the soil to give the measured and calculated ionic concentrations. [7]

| Species | Equilibrium Concentration in Solution (mM) | Concentration in Soil (wt %) |
|-------------------------------|--|------------------------------------|
| CaCO ₃ (calcite) | saturated | 3-5 |
| MgCO ₃ (magnesite) | saturated | ≤ 1.8 |
| MgSO ₄ (epsomite) | dissociated | 3.3 |
| ClO ₄ ⁻ | 2.5 | 0.6 |
| Na ⁺ | 1.4 | 0.08 |
| Cl ⁻ | 0.40 | 0.04 |
| K ⁺ | 0.40 | 0.04 |
| Mg ²⁺ | 6.4 | — |
| SO ₄ ²⁻ | 3.9 | — |
| HCO ₃ ⁻ | 5.4 | — |
| MgSO ₄ (aq) | 1.2 | — |
| Ca ²⁺ | 0.75 | — |
| CaSO ₄ (aq) | 0.17 | — |

of the Mars Rovers that the surface of Mars was acidic in nature, however, wet chemistry of the soil has revealed a slightly alkaline pH, at least in the north polar regions of the planet. [6]

The discovery of 0.6 wt. % perchlorate in the Martian soil was a big surprise. In fact, the majority of chloride found by WCL was in the form of perchlorate. It has been suggested the parent salt on Mars is in the form of Mg(ClO₄)₂ or Ca(ClO₄)₂ due to the distribution of cations also present in the soil. These salts have a high affinity for water, are deliquescent, and have a eutectic freezing point in the range of -70 °C. [19] The presence of perchlorate on Mars has implications about the potential for liquid water on the planet under present day temperature and pressure. Through experimental measurements and thermodynamic and kinetic calculations, it has been shown the magnesium perchlorate present in the soil is capable of substantially lowering

the freezing point of water on Mars, suggesting the possibility of the presence of metastable liquids at the Phoenix landing site. [29]

The presence of perchlorate in such quantities in the soil also has an impact on the potential presence of organics on Mars and the ability of past and/or future missions to detect organics. Though perchlorate is not readily able to oxidize organics under Martian conditions, its presence does suggest oxidizing formation chemistry in the Martian atmosphere or on the Martian surface depending on the mechanism of perchlorate formation, which is still under debate (for more information see Chapter 3). Likewise, perchlorate is capable of oxidizing organics under the high temperature conditions of the pyrolytic experiments which were performed by the Viking missions and also by Phoenix's TEGA instrument. It has been proposed that the presence of perchlorate in the soil was responsible for the negative result for organics, prompting studies on the effect of perchlorate on organic detection and alternative methods for detecting Martian organics. [19] For more about organic detection on Mars and the effects of perchlorate on analysis see Chapter 6.

In addition to the presence of high levels of perchlorate, another interesting discovery was the lack of high levels of sulfur expected to be present from the findings of previous missions. Previous missions have reported concentrations of sulfate from 4 to 8 wt. % SO_3 , yet with wet chemistry experimentation $\sim 1.1(\pm 0.5)$ wt. % was calculated. Additionally, the S/Cl ratio has previously been reported as $\sim 4:1$ but given the concentration of SO_4^{2-} , Cl^- and ClO_4^- measured by WCL the ratio is only $\sim 2:1$. It has been suggested the discrepancy may be the result of non-soluble or sparingly soluble forms of sulfur measured by XRF in previous missions which could not be measured by WCL thus lowering the S/Cl ratio. [7]

Three small (1 cm^3) sampling areas were examined, one at the surface and

two at a depth of 5 cm at the top of the ice table. All three samples gave, within error, similar concentrations of ions, pH and conductivity, which suggest the soil is fairly homogenous, at least in the region analyzed. [7] However, it is important to remember when discussing the results of the WCL experiments on Mars that sampling was limited to a very small area of a planet with diameter of 6,778 km (intermediate in size between Mercury and Earth) and surface area nearly equivalent in size to the land area of Earth. [17] Therefore, it would not be wise to extrapolate the finding of the WCL to the entire surface of the planet Mars. There is no evidence to suggest the chemistry of Mars is homogeneous. However, it is prudent to use the results for WCL, as well as TEGA and the other instruments aboard Phoenix, to continue to better the understanding of the Martian soil. This new information is useful in helping to determine a suitable Mars analog soil on Earth. This soil can then be used in the testing of new instrumentation for Mars exploration allowing for superior analysis of the Martian soil in future missions so the chemistry of Mars will one day be fully understood.

2 Analysis of Soils from the McMurdo Dry Valleys

2.1 Introduction

In Chapter 1, the calibration and characterization of the Wet Chemistry Laboratory (WCL) instruments aboard the 2007 Phoenix Mars Scout Lander was discussed. However, there is one additional step in the C, C and C process: cataloging. Cataloging is the process of collecting an instrument response library for comparison to the data collected during the actual mission. It is imperative when cataloging an instrument's response to use samples that as closely as possible resemble the samples likely to be encountered during the actual mission. Determining the proper samples to be used as Mars analog soils is difficult. From the Viking missions, it has been shown there are strong similarities between the environment on Mars and the environment of the McMurdo Dry Valleys. Some of the similarities include: a low mean temperature, strong winds, lack of rain and little snowfall, daily freeze-thaw cycles, low humidity, and the presence of salts in the soil. [30] These similarities suggest the soils from the MDV could provide a suitable Mars analog. In fact, many consider the MDV to be the most Mars-like place on Earth. [30, 31, 32, 33, 34]

Fortuitously, the launch of the Phoenix Mission coincided with the International Polar Year (IPY). IPY was a scientific program from March 2007 to March 2009 focusing on the study of Earth's polar regions: the Arctic and Antarctic. As part of the IPY, six members of the Phoenix team visited the McMurdo Dry Valleys in Antarctica to test some of the Phoenix instruments, including WCL, *in-situ* on soil samples. Many additional soil samples were gathered to be analyzed back in the laboratory in an effort to catalog WCL responses to a variety of Mars analog soils from the MDV. [3]

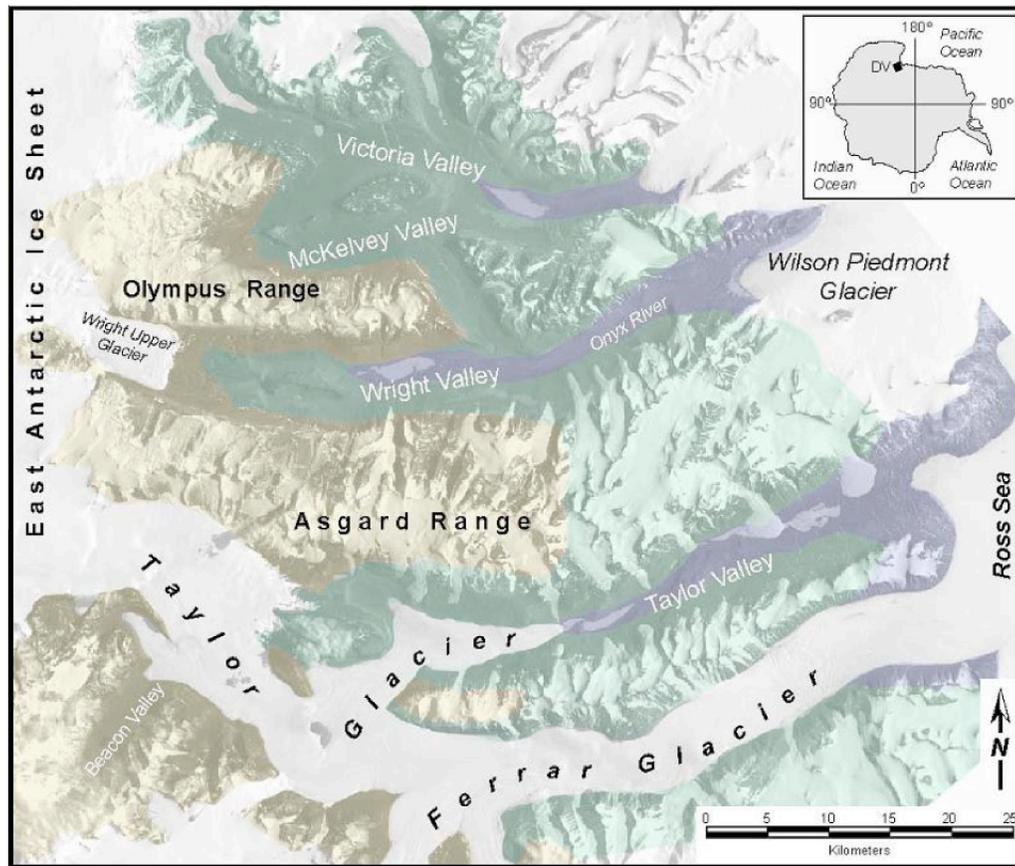
The purpose of analyzing soil from the MDV was two-fold. In addition to cataloging samples for comparison to the Phoenix results, the results from the analysis would also further our understanding of the MDV as a unique soil environment on Earth. This analysis allowed for an investigation of the chemical and physical characteristics of the soil and ice in the McMurdo Dry Valleys (MDV) as a function of valley elevation and soil depth. [3]

This chapter will provide a background of the physical characteristics of the McMurdo Dry Valleys which leads them to being a good Mars analog environment. This is followed by the experimental parameters for the study of the soils of the MDV in the laboratory using a variety of complementary instrumentation to determine the pH, electrical conductivity, ionic strength and soluble ionic species present in the soils. This chapter will conclude with a discussion of the results and a comparison of the MDV Mars analog soils to the results of the WCL analysis of the actual Martian soil.

2.2 Background

The McMurdo Dry Valleys (MDV) are the largest snow-free region of Antarctica. Measuring approximately 4000 km², 0.03% of the continent of Antarctica, the MDV cuts inland from the Ross Sea from east to west toward the ice cap of the polar plateau (Figure 10). This region is known as a cold desert. The annual mean temperature of this region is -20°C and averages 45 mm or less of water-equivalent precipitation, only in the form of snow, making it a hyperarid region. [35]

Salt Accumulation: Like in other arid regions, due to the limited precipitation there is an accumulation of salts in the MDV. Salts in the MDV accumulate in soil horizons. Soil horizons are parallel layers in the soil pro-



Upland Stable Zone Inland Mixed Zone Coastal Thaw Zone

Figure 10: Map of the McMurdo Dry Valleys of Antarctica. The Dry Valleys are divided into the three microclimate zones: upland stable zone, inland mixed zone and coastal thaw zone. Valleys discussed in this text include: Taylor Valley, Wright Valley, Victoria Valley, Beacon Valley. University Valley (not labeled in map) is a small valley off the side of Beacon Valley. Adapted from Figure 2 in [34].

file with distinctive chemical and physical characteristics which differ from the layers directly above or below. Each soil horizon is classified based upon these chemical and physical characteristics. When determining a soil's chemical profile, samples are typically taken from all soil horizons present from the pavement (top most layer) to the frozen ground, also referred to as permafrost or ice-cement.³ [35]

Proposed sources for the salts present in the MDV include atmospheric precipitation, rock weathering, and direct marine origin. Figure 11 shows a flow chart with possible pathways for the origin of salts in the MDV of Antarctica.

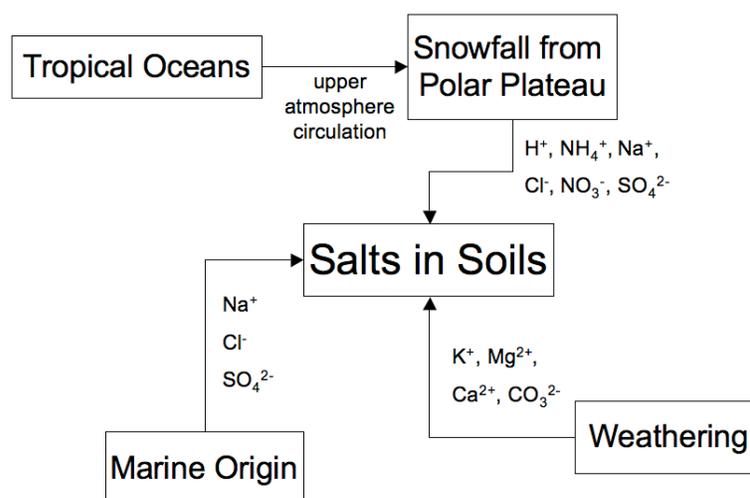


Figure 11: Pathways of Salt Accumulation in the Soils of the McMurdo Dry Valleys, Antarctica. Modified from [35]

As seen in Figure 11, atmospheric precipitation (*i.e.*, snowfall) from the Polar Plateau brings $(\text{NH}_4)_2\text{SO}_4$, HNO_3 , and NaCl to the soils, while the oceans contribute NaCl and Na_2SO_4 , and rock weathering provides the additional

³The three terms: frozen ground, permafrost and ice-cement all have slightly different definitions, which can be found in Appendix B but for consistency the term permafrost will be used throughout this work to refer to the layer of soil that is permanently frozen whether with or without ice.

cations of K^+ , Ca^{2+} , and Mg^{2+} and the anion CO_3^{2-} . The salts in the MDV consist mainly of the anions: Cl^- , NO_3^- , and SO_4^{2-} and the cations: Na^+ , K^+ , Ca^{2+} and Mg^{2+} , as determined by prior works. [35, 36, 37, 38]

Microclimate Zones: While each of these ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) is typically present in all soil horizons of all MDV soils, the salt composition varies depending on location and climate conditions. The MDV can be divided into a series of microclimate zones based upon variations in weather patterns. Each zone is distinguished by elevation, aridity, amount of precipitation/moisture, depth to permafrost, salt composition, salt concentration, and type of patterned ground present. [35] Different subdivisions have been proposed. [34, 35, 38] Marchant and Head [34] distinguish three microclimate zones, a coastal thaw zone (CTZ), an inland mixed zone (IMZ) and a stable upland zone (SUZ), shown in Figure 10, which capture the major trends in landscape features across the MDV.

Coastal Thaw Zone: The coastal thaw zone (CTZ) is located at low elevations of 100-1000 m, 30-40 km from the coast. The main valley in this zone is Taylor Valley. The lower elevation and proximity to the coast means this climate zone has the most moisture. In this zone the mean annual air temperature averages around $-17^\circ C$, the relative humidity is $\sim 64\%$, and snowfall exceeds 80 mm of water-equivalent per year. [34] The melting of summer snowfalls and glaciers moisten the ground resulting in liquid water in the soil for part of the year. The higher moisture level is evident in the numerous pools, streams and lakes present in this zone. The increased moisture in this region means there are much thinner soil horizons, along with more rock weathering and soil leaching. The increased leaching means this zone contains the least amount of soluble salts present in the soil. However, salts are still present,

mostly sodium chloride and sodium sulfate which are the result of marine aerosols. [35]

The depth to the ice table is typically shallow in this zone, <45 cm.⁴ [35] Patterned ground in the form of ice-wedge polygons are present in the coastal thaw zone. The alternative freezing and thawing of liquid water results in thermal contraction of the soil forming these geological features. These polygons typically measure ~10-20 meters in diameter and have wedges with a maximum width of ~2 meters. [34]

Inland Mixed Zone: The inland mixed zone (IMZ) is the largest of the three microclimate zones and is located between the stable upland zone and coastal thaw zone at moderate elevations and ranges from the edge of the inland ice sheet to the coastal mountains. Valleys in this zone include: Wright, McKelvey, and Victoria Valleys. The inland mixed zone is more arid than the coastal thaw zone with mean annual air temperatures ranging from -21 to -30°C, slightly higher relative humidity of ~67% and an indeterminate amount of precipitation. The difficulty in determining the amount of precipitation comes from the uncertainty in the quantity of wind blown snow from the polar plateau which enters this zone. Moisture in the inland mixed zone comes from summer snowfalls, which can moisten the soil surface as well as enter the subsurface as water vapor. The moisture in this zone (still less than 10%) allows for some leaching of soluble salts, similar to the salts found in the coastal thaw zone, resulting in less well defined soil horizons. It also contributes to more rock weathering. [35, 34]

Depth to the ice table typically averages 35-70 cm.⁵ [35] Polygons are also

⁴The depth to the permafrost ranged from 28 to 34 cm in the four locations where pits were dug for this study (see Appendix C).

⁵The depth to the permafrost ranged from 19 to 27 cm in the three locations where pits were dug for this study (see Appendix C).

present in the inland mixed zone. There are two types of polygons found in this zone: sand-wedge and composite. Sand-wedge polygons are closely related to the ice-wedge polygons seen in the coastal thaw zone but contain troughs filled with stratified sand and gravel instead of ice. Composite polygons contain wedges that alternate between sand and ice. [34]

Stable Upland Zone: The stable upland zone (SUZ) is located at high altitudes adjacent to the Polar Plateau. [35] Valleys in this zone include, Arena, Beacon and University Valleys, among others. This zone is the most arid, with mean annual air temperatures of below -30°C , a relative humidity of $\sim 41\%$, and limited snowfall. Snow, which is windblown from the polar plateau, sublimates on the soil surface rather than melting. The lack of moisture in the soil ($<3\%$), does not allow for much leaching to occur and results in the presence of thick and well defined soil horizons containing highly soluble salts. [34]

Additionally, the ice table is the most deep in this zone and is present beneath a layer of dry permafrost.^{6,7} Dry permafrost is unique to the high elevations of the McMurdo Dry Valleys [39] and it is not found in the arctic or any other deserts on Earth.⁸ [40] Accumulation of salts in this zone is believed to result from the sublimation of snow as well as from rock weathering. The result of this accumulation is the presence of Na^+ , Ca^{2+} , Mg^{2+} , NO_3^- , and SO_4^{2-} in the soil with little Cl^- present. [35, 34] As with the other microclimate zones, the stable upland zone also contains polygons. In this

⁶The depth to the permafrost 19 to 34 cm in three of the four locations were pits were dug for this study. In the fourth location a pit was dug to 105 cm and a permafrost layer was not reached (see Appendix C).

⁷There are several definitions of the term dry permafrost. (see Appendix B)

⁸Deep active layers in coarse-textured sediments are often mistaken for dry permafrost. Reports of dry permafrost in the High Arctic is an example of this confusion. The difference between dry permafrost and a deep active layer can only be determined by monitoring the soil temperature continuously for ≥ 2 years. [40]

zone, it is the sublimation of subsurface ice which creates these polygons, called sublimation polygons. [34] These polygons measure 10 to 20 meters in diameter and typically have a 3 meter height difference between their center and the trough. [41]

Similarities of MDV and Mars: There are many similarities between the McMurdo Dry Valleys of Antarctica and Mars which make the MDV a suitable Mars analog environment. Both are classified as hyperarid, cold deserts. Mars is globally hyperarid while the stable upland zone of MDV is hyperarid and the aridity lessens in the inland mixed and coastal thaw zones. In the MDV, the climate is divided into three microclimate zones each with different mean temperatures. Likewise, Mars exhibits differences in mean annual surface temperature at varying latitudes. In both environments the presence of ground ice and depth to the ice table is dependent on the microclimate zone.

There are also similarities in appearance for these two environments. (see Figure 12). The soils on both planets contain soluble salts. These soluble salts have the ability to form brines which can affect the temperature at which liquid water freezes.

The soils are also patterned.⁹ Contraction-crack polygons are present in all three microclimate zones, formed by thermal cracking of ice-rich permafrost. The cracks are then filled with a variety of materials. [34] Mars is also patterned with polygons. The polygons on Mars are concentrated at latitudes above $\sim 50^\circ\text{N}$ and 50°S and can be up to five times larger in size than those in the MDV. The larger size is believed to come from either deeper cracks due to lower temperatures or larger temperature variations. [34] While there is a large range of sizes for the polygons on Mars, the most abundant type measures 15-40 meters in width which is similar in size to those in the MDV. As in

⁹A definition of patterned ground can be found in Appendix B.

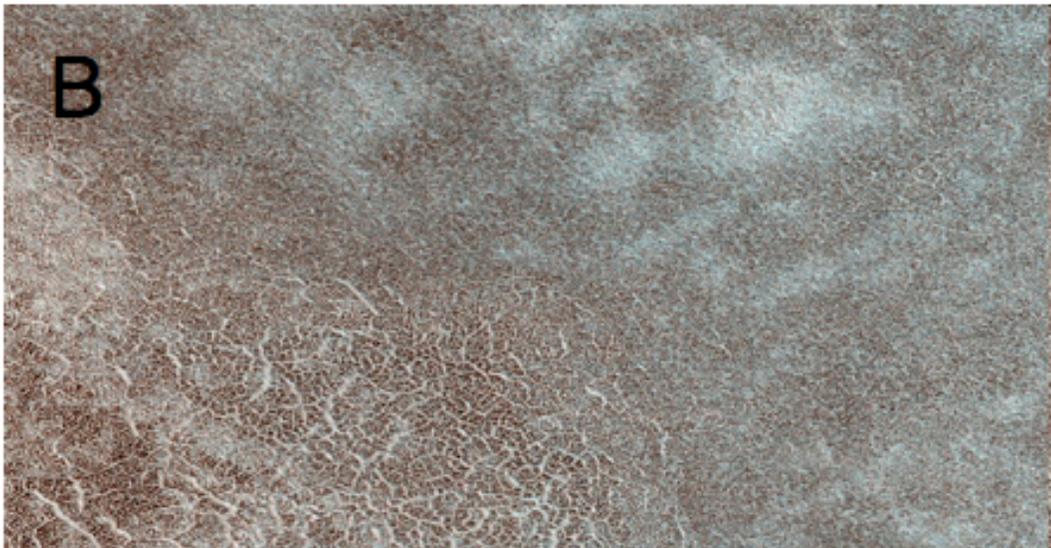


Figure 12: Comparison of: (A) the McMurdo Dry Valley (MDV) landscape [42] to (B) the Martian Landscape at the Phoenix Mars Lander site [43]

the MDV the polygons on Mars are believed to be determined by microclimate zone. Ten different subsets of polygons have been characterized on Mars including all four types seen in the MDV: ice-wedge, sand-wedge, composite, and sublimation. As in the MDV, the polygon type can offer clues about climate and microclimate changes. [34]

Polygons are just one type of surface topography that MDV and Mars share. When looking at the topography of both places it is possible to see similarities on all three scales: macroscale, mesoscale and microscale. Table 17 lists a variety of similarities on all three scales. For more information more about these similarities see Marchant and Head (2007). [34]

Table 17: Landforms present in the MDV and on Mars [34]

| Landform Scale | Size (m) | Landform Type |
|----------------|-----------|--|
| Macroscale | >250 | Slope asymmetry Drainage-basin asymmetry Gullies |
| Mesoscale | 1 to ~250 | Contraction-crack polygons Viscous-flow features |
| Microscale | >>1 | Tafoni Weathering pits Desert pavement Duricrusts |

Another similarity between the Phoenix’s landing site on Mars and the stable upland zone in the MDV is the presence of dry permafrost and subsurface ground ice in both environments. Both environments have a similar subsurface profile with a layer of dry permafrost above a layer of ice-cemented ground. The ground ice in both environments is charged and discharged not with liquid water but rather with vapor exchange, due to the lack of liquid water present in either location. Likewise, it is possible for the top of the ground ice to exceed 0°C. [44]

However, there are also some large differences between the two environ-

ments. The mean surface annual temperature on Mars is 25-50°C colder than the coldest regions of the stable upland zone of the MDV averaging approximately -58°C. Though the MDV are bombarded with high levels of UVB and UVC radiation [45], this solar radiation does not penetrate as deep through the atmosphere to interact with the soils as it does on Mars. Also, the total atmospheric pressure hovers around the triple point of water on Mars, while it is largely exceeded on Earth in the MDV. [34] Despite these differences, some believe there is no place on Earth as similar an environment to Mars as the MDV. [30, 31, 32, 33, 34]

2.3 Experimental

2.3.1 Collection of McMurdo Dry Valley Soils

As part of the International Polar Year, soils from the McMurdo Dry Valleys were analyzed *in-situ* as well as collected to be analyzed in the laboratory. The soil samples came from various locations scattered throughout the MDV's three microclimates zones. Bulk soil samples were collected from 11 sampling sites located throughout five valleys: Beacon, Taylor, University, Victoria and Wright (Table 18).

At each site, a pit was dug from the pavement to the permafrost exposing an area of about 0.5 m². The various soil horizons were identified using standard methods (“Soil Survey Laboratory Methods Manual”, USDA, 2004; <http://soils.usda.gov/technical/lmm/>). Sterile tools were then used to collect about 2 kg soil samples from each horizon from the bottom up to avoid cross contamination. The permafrost was also sampled with a sterile hammer and chisel. All samples were stored, shipped and maintained in a frozen state until the time of analysis. A total of 44 soil samples and 17 permafrost samples were collected and analyzed. A complete list of soils can be found in Appendix C.

Table 18: Location and characteristics of sampling sites in the MDV

| Valley | Pit # | Latitude | Longitude | Elevation (m) |
|-----------------|-------|-------------|--------------|---------------|
| Taylor | 1 | S77 36 06.1 | E163 08 19.2 | 21 ± 5.5 |
| Taylor | 2 | S77 36 06.1 | E163 08 19.6 | 21 ± 5.5 |
| Taylor | 4 | S77 35 59.9 | E163 08 00.4 | 41 ± 4.9 |
| Taylor | 3 | S77.35 43.8 | E163 07 23.4 | 108 ± 5.5 |
| Upper Wright | 13 | S77 30 45.9 | E161 09 17.6 | 182 ± 5.9 |
| Middle Victoria | 8 | S77 22 28.8 | E161 48 29.9 | 357 ± 5.8 |
| Middle Victoria | 9 | S77 22 05.3 | E161 48 56.5 | 394 ± 5.2 |
| Lower Beacon | 11 | S77 49 29.1 | E160 38 34.1 | 1209 ± 6.4 |
| Upper Beacon | 20 | S77 49 49.5 | E160 38 58.5 | 1240 ± 5.6 |
| University | 7 | S77 51 43.6 | E160 42 23.8 | 1683 ± 5.9 |
| University | 10 | S77 51 52.9 | E160 43 40.2 | 1703 ± 5.5 |

2.3.2 Soil Preparation

In the laboratory, the soil and permafrost samples were prepared for analysis. All permafrost samples were weighed, dried in a dessicator and re-weighed to determine the percentage of water in each sample. All soil samples were homogenized by pulverization with a mortar and pestle to a particle size of <600 microns. This step was performed to ensure each sample analyzed was an accurate representation of the total sample. Homogenization also allowed for ions trapped in larger particles the opportunity to leach into solution in a reasonable timeframe. After homogenization, soil samples were further prepared depending on the method of analysis.

2.3.3 Soluble Ion Analysis

Soil samples from the McMurdo Dry Valleys were analyzed for a variety of water-soluble species. Soil samples from all 11 pits from the three climate zones listed in Table 18 were analyzed for Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , Br^- , ClO_4^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} by ion chromatography (IC) and CO_3^{2-} and HCO_3^- by acid-base titration. Additionally, a subset of these

soils, from Pits 1 and 2 in Taylor Valley in the coastal thaw zone and Pits 7 and 10 in University Valley in the stable upland zone, were also analyzed for Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , NO_3^- , and SO_4^{2-} using the ion selective electrodes (ISEs) in the wet chemistry laboratory (WCL) testbeds designed for the analysis of the Martian soil during the Phoenix Mars mission (see Chapter 1). Each method of water-soluble ion analysis, including any additional soil preparation associated with that analysis is discussed below.

Ion Chromatography Procedure: For analysis by ion chromatography (IC), a 1:25 weight ratio of soil to water was used for the extraction of the water-soluble species. One gram of homogenized soil was added to 25 mL of 18.2 m Ω water. The solution was shaken for 30 seconds and leached for ~24 hours at room temperature. The solution was filtered through a 0.2 μm filter prior to analysis.

A pair of Dionex ICS-2000s reagent-free ion chromatographic systems (Dionex, Sunnyvale, CA, USA) set-up to run anions and cations simultaneously were used to determine the major soluble ions in leached soil solutions. Each system included a dual-piston pump, a high-pressure injection valve with a 25- μl sample loop, Dionex DS6 heated conductivity cell and an AS40 automated sampler (Dionex) with which all samples were loaded.

For the anions, a Dionex Ionpac AS18 analytical column (250 x 4 mm I.D.) and a AG18 guard column (50 x 4 mm I.D.) were used along with an Anion Self-Generating Suppressor 300 (4-mm). The eluent was 23 mM potassium hydroxide with a flow rate of 1.0 ml/min. For the cations, a Dionex Ionpac CS12A analytical column (250 x 4 mm I.D.) and a CG12A guard column (50 x 4 mm I.D.) were used along with an Cation Self-Generating Suppressor 300 (4-mm). The eluent was 20 mM methanesulfonic acid with a flow rate of

1.0 ml/min. The data was collected and analyzed using the software package Chromeleon.

A multi-ion cation standard solution containing: Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , and Ba^{2+} was diluted to prepare a range of cation standards for calibration of the cation IC. A multi-ion anion standard solution containing: Cl^- , Br^- , SO_4^{2-} , NO_3^- , and PO_4^{3-} was diluted to prepare a range of standards for calibration of the anion IC. Tables 19 and 20 list the concentration (in μM) of each cation and anion in each standard.

Table 19: IC cation standards used for the analysis of MDV soils

| | Standard 1 | Standard 2 | Standard 3 |
|------------------|-------------------|-------------------|-------------------|
| Cation | (μM) | (μM) | (μM) |
| Li^+ | 2.9 | 14.4 | 72.0 |
| Na^+ | 3.5 | 17.4 | 87.0 |
| NH_4^+ | 5.5 | 27.7 | 138.6 |
| K^+ | 5.1 | 25.6 | 127.9 |
| Mg^{2+} | 20.6 | 41.1 | 102.9 |
| Ca^{2+} | 5.0 | 25.0 | 124.8 |
| Ba^{2+} | 2.9 | 5.8 | 14.6 |

Table 20: IC anion standards used for the analysis of MDV soils

| | Standard 4 | Standard 5 | Standard 6 |
|--------------------|-------------------|-------------------|-------------------|
| Anion | (μM) | (μM) | (μM) |
| Cl^- | 1.4 | 14.1 | 28.2 |
| Br^- | 1.3 | 12.5 | 25.0 |
| NO_3^- | 1.6 | 16.1 | 32.3 |
| SO_4^{2-} | 1.0 | 10.4 | 52.1 |
| PO_4^{3-} | 1.6 | 15.8 | 31.6 |

Each day a sequence was run consisting of three cation calibration standards, three anion calibration standards, and a 500 μL aliquot of each soil sample in numerical order. Blanks of 18.2 m Ω water were run at the beginning of the sequence between the two sets of calibration standards and between the calibration standards and samples as a quality control measure. The Dionex

program used ran for a total of 32.5 minutes for each sample with 30 minutes for analysis and 2.5 minutes between samples for the autosampler to relay the solution to the IC systems.

Initially, the samples were run in triplicate without dilution. However, the concentrations of some of the ions were well above the concentration of the standard solution making accurate interpretation impossible. Accordingly, the samples were diluted 1:10 or 1:100 and run in triplicate.

Acid-Base Titration Procedure: Due to the nature of ion chromatography, it is difficult to quantify soluble carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-). Therefore, it was necessary to use a different experimental method for the determination of CO_3^{2-} and HCO_3^- . These compounds were determined by acid-base titration with ~ 0.01 N (~ 0.05 M) sulfuric acid solution to pH 8.3 for CO_3^{2-} and 4.5 for HCO_3^- .

To prepare the sulfuric acid solution, 14 mL of concentrated (98%) sulfuric acid was diluted in 18.2 mL water to 500 mL creating a solution of ~ 1 N (0.5 M) H_2SO_4 . This solution was then diluted 100-fold (20 mL in 2 L volume) to obtain ~ 0.01 N H_2SO_4 . The sulfuric acid solution was then standardized with a standard solution of NaOH, which had previously been standardized with potassium hydrogen phthalate (KHP). The standardized solution of sulfuric acid had a concentration of 0.0123 N H_2SO_4 .

For analysis by acid-base titration, a 1:25 weight ratio of soil to water was used for the extraction of the soluble carbonate and bicarbonate. Two grams of homogenized soil was added to 50 mL of 18.2 mL water. The solution was shaken for 30 seconds and leached for ~ 24 hours at room temperature. The solution was filtered through a 0.2 μm filter prior to analysis.

To perform the titration, 10 mL of soil leachate solution was added to a 50

mL Erlenmeyer flask. One drop of 1% phenolphthalein indicator was added to the flask. If pink color appeared, the leachate solution was titrated with the standardized $\text{H}_2\text{SO}_4^{2-}$ solution until the color disappeared. This was the first endpoint and was used to determine the amount of carbonate present in the leachate. Then two drops of 0.1% methyl orange indicator was added to the leachate solution turning it yellow in color. The titration then continued until the color turned to orange. This was the second endpoint and was used to determine the amount of bicarbonate present in the leachate. For each soil leachate, four titrations were performed, one fast and three slow. Additionally, four titrations, one fast and three slow, of a blank (18.2 m Ω water only) were also performed. The blank solution was subjected to the exact same procedure as the soil leachate solutions minus the filtration through the 0.2 μm filter.

Wet Chemistry Laboratory Procedure: For analysis in a WCL testbed, a 1:25 weight ratio of soil to leaching solution was used for the extraction of the water-soluble species. One gram of homogenized soil was added to 25 mL of leaching solution. The leaching solution used was TS21 (see Table 2 in Chapter 1 for the concentration of ions in this solution). The soils were shaken for 30 seconds and leached for \sim 24 hours at room temperature. The solution was then filtered through a 0.2 μm filter before analysis.

ISE analysis was performed in a WCL testbed (Figure 2) containing both solid state and PVC-membrane ISEs. (For a full list of sensors see Table 1.) The WCL array is capable of determining the concentration of Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Cl^- , and $\text{NO}_3^-/\text{ClO}_4^-$ along with total conductivity. At the start of each new day of analysis, the testbed was removed from the refrigerator and soaked for minimum of one hour with 25 mL of TS20. Table 2, in Chapter 1, lists the composition of TS20-TS24 (in M). The WCL testbed

was then calibrated using the spiking method discussed in Chapter 1.

After calibration, the testbed was rinsed three times with 18.2 m Ω water and once with TS20 before being filled again with 25 mL of TS20. The stirrer and sensors were turned on and the TS20 data was collected for 10 minutes which allowed time for the solution to equilibrate. Then the solution was spiked to TS21. Once the solution equilibrated and data was collected for five minutes, it was aspirated out of the cell and replaced with 20 mL of the sample solution. This solution was allowed to equilibrate and data was collected for around 15 minutes. If more than one sample was run per day, the testbed was rinsed three times with 18.2 m Ω water and once with TS20 before 25 mL of TS20 was added and the process repeated. All data collection for both calibrations and samples was performed on a desktop or laptop computer using specifically customized LabView software.

To test the viability of using the WCL ISEs as a comparative soluble ion analysis technique to ion chromatography, a sample of a known quantity of NaCl was run in both systems back-to-back. The testbed was filled with TS20 solution and the stirrer and sensors were turned on to collect data for 10 minutes. Then the solution was spiked to TS21. Once the solution equilibrated, and data was collected for 5 minutes, it was aspirated out of the cell and replaced with 25 mL of a TS21 solution to which additional NaCl had been added to raise the concentrations of Na⁺ and Cl⁻ by \sim 50 mM and leaving all other ions at the same concentrations. This solution was run for 1 hour in WCL and then taken from the testbed, filtered through a 0.2 μ m syringe filter and run in the IC along with aliquots of both TS20 and TS21. The results from both analyses were then compared to determine how closely the concentrations of Na⁺ and Cl⁻ matched for each analysis.

2.3.4 pH, Conductivity and Ionic Strength Analysis

In addition to the analysis of soil for water-soluble ions, the soil leachate solutions were also analyzed for pH, conductivity, and ionic strength. As with the IC analysis, further soil preparation was necessary. A 1:25 weight ratio of soil to water was used to for the extraction of soluble ionic species. One gram of the homogenized soil was added to 25 mL of 18.2 m Ω water. The solution was shaken for 30 seconds and leached for one hour at room temperature. The solution was filtered through a 0.2 μ m filter prior to analysis. The leached solution was stored in a tightly sealed glass vial on the benchtop until analyzed. Further details of each analysis are discussed below.

pH of MDV Soils: The pH of all MDV soil leachates were measured with a commercial pH probe (Thermo Fisher Scientific ORION 3-Star pH Meter). Measurements were taken in triplicate at room temperature. The pH probe was calibrated each day prior to analysis with commercial premixed buffer solutions of pH 4, 7 and 10 and the slope value was determined.

Conductivity of MDV Soils: The total conductivity of all leached MDV soil leachates were determined by measurement with either a commercial Orion conductivity probe (for Pit 20) or an external conductivity probe connected to the WCL electronics (for all other pits). Measurements were taken in triplicate at room temperature. Regardless of which conductivity probe was being used, it was calibrated prior to analysis with solutions of 100 μ S/cm, 1413 μ S/cm and 12.9 mS/cm KCl and the cell constant was determined.

When using the commercial Orion conductivity probe, the probe was placed in solution until the reading stabilized. The solution electrical conductivity was recorded in units of μ S/cm. Measurements were taken in triplicate at

room temperature. When using the external conductivity probe connected to the WCL electronics, the probe was placed into solution and the conductivity was recorded for five minutes. The average conductivity was then determined disregarding the first 30 seconds and last 30 seconds of data collected. The conductivity was then converted to solution electrical conductivity (in $\mu\text{S}/\text{cm}$) using the calibration curve produced prior to sample analysis.

Ionic Strength of MDV Soils: The ionic strength (μ) of each soil leachate solution was calculated for each soil sample using two separate methods. In the first method (μ_{exp}), the ionic strength was calculated as the sum of the concentration of all ions in solution determined by ion chromatography and acid-base titration (Equation 7):

$$\mu = 1/2 \sum_{i=1}^{\infty} c_i z_i^2 \quad (7)$$

where c_i is the molar concentration of ion i in (M) and z_i is the charge number of that ion. In the second method (μ_m), the ionic strength was calculated from the electrical conductivity using Equation 8:

$$\mu = 0.0127\text{EC} \quad (8)$$

where EC is the electrical conductivity (in dS/m). Ideally, if all ions present in the soil leachate solution were identified and quantified by the IC and acid-base titrations, the results of Equations 7 and 8 would be identical. However, it is unlikely that all ions will be accounted for experimentally and therefore it is often found $\mu_m > \mu_{exp}$.

An In-depth Look at Ionic Strength: The discrepancy in the ionic strength data for the inland mixed zone and stable upland zone prompted a closer look as to how the ionic strength of solutions from soil extracts are calculated. Equation 8 is known as the Griffin-Jurinak Relationship. Griffin and Jerinak [46] measured the ionic strength and electrical conductivity of natural aqueous solution, river waters and soil extracts and determined a linear relationship between the two parameters with a slope of 0.0127 and an R^2 of 99.6%. This relationship holds for soil extracts with both low and high electrolyte concentrations dominated by monovalent ions, Cl^- and Na^+ . Thus, we expect that Equation 8 will work well for soils from the coastal thaw zone but not the inland mixed zone of the stable upland zone. The coastal thaw zone is close to the ocean and therefore soils in this zone are dominated by Na^+ and Cl^- from marine aerosols. However, soils from the inland mixed zone and stable upland zone are further inland and therefore have smaller concentrations of Na^+ and Cl^- . In fact soils from these zones are dominated by divalent salts such as Ca^{2+} and SO_4^{2-} .

The Griffin-Jurinak Relationship has been found to give variable results according to the concentration and type of ions present in solution. To account for this discrepancy, variations of the constant in the Griffin-Jurinak Relationship (0.0127) have been proposed when soil samples with varying concentration and types of ions have been tested. [47] For this reason, a study was performed to determine a new constant for the Griffin-Jurinak Relationship suitable for the MDV soils from the inland mixed and stable upland zones.

Using the concentration of each ion present in a representative soil sample from University Valley Pit 7 (ANUV0726) which had the highest ionic strength of all soils tested, a new set of conductivity standards was prepared. The ions were paired as best as possible, but it was difficult to have a perfect pairing

due to charge imbalance. Therefore, higher concentrations of Cl^- , SO_4^{2-} and NO_3^- were used to balance the charge (Table 21). Carbonate was not used in the charge balance because this soil had a slightly acidic pH of 6.54 ± 0.11 and the soil was found to contain no carbonate and only a small concentration of bicarbonate.

Table 21: Concentration of each salt present in the highest ionic strength conductivity standard prepared to match as closely as possible the concentration of each ion in MDV sample ANUV0726 for the determination of a new slope value for the Griffin-Jurinak Relationship

| Salt | Concentration (M) |
|-----------------------------|-------------------|
| CaSO_4 | 3.31E-3 |
| NaCl | 2.25E-3 |
| $\text{Mg}(\text{ClO}_4)_2$ | 1.27E-7 |
| $\text{Mg}(\text{NO}_3)_2$ | 1.97E-3 |
| NH_4NO_3 | 7.96E-6 |
| KNO_3 | 1.15E-4 |

The multi-ion solution was then diluted 1.25, 2.5, 5 and 10-fold. Table 22 lists the ionic strengths for all five solutions. Five more solutions were also

Table 22: Concentration of of Solutions in a series of conductivity standards prepared to determine a new slope value for the Griffin-Jurinak Relationship

| Solution (#) | μ (M) |
|--------------|-----------|
| 1 | 2.16E-3 |
| 2 | 4.32E-3 |
| 3 | 1.08E-2 |
| 4 | 1.73E-2 |
| 5 | 2.16E-2 |

prepared with the same ionic strengths listed in Table 22 but containing only a single ion pair, Na^+ and Cl^- .

The Orion conductivity probe was calibrated with commercially available conductivity standards (100 $\mu\text{S}/\text{cm}$, 1413 $\mu\text{S}/\text{cm}$ and 12.9 mS/cm KCl solutions). The electrical conductivity of the prepared standards was then mea-

sured. The ionic strength was plotted versus the conductivity for the multi-ion standards and the single ion standards.

2.4 Results and Discussion

Soil samples from the McMurdo Dry Valleys were analyzed for a variety of water-soluble species, by ion chromatography (IC), acid-base titration, and the ion selective electrodes (ISEs) in the wet chemistry laboratory (WCL). Additionally, the pH, conductivity and ionic strength of the soil samples was also determined. Results from these analyses will be discussed along with a comparison of soils from in each of the three climate zones. This will be followed by a comparison of soils from two of these climate zones, the coastal thaw zone and stable upland zone, to the soil from the northern polar region of Mars at the Phoenix landing site (Chapter 1) to determine which climate zone in the MDV contains the better analog soils, closer in chemical composition, to the soils on Mars.

2.4.1 Soluble Ions

Soil samples from 11 pits scattered across the three climate zones in McMurdo Dry Valleys (see Table 18) were analyzed by ion chromatography (IC) and acid-base titration for a variety of water-soluble species. IC was chosen as the method of choice for soluble ion analysis because it is capable of detecting a wide range of anions and cations allowing for a more complete analysis. The IC analysis was supplemented with acid-base titration for the detection and quantification of carbonate and bicarbonate due to the difficulty of quantifying these species with IC. A discussion of the results divided into the three climate zones: coastal thaw, inland mixed, and stable upland.

In addition, soils from two pits in the coastal thaw zone (Pits 1 and 2)

and two pits in the stable upland zone (Pits 7 and 10) were also analyzed for soluble ions by the ISEs in the WCL, the instrument which performed the analysis of the Martian soil (see Chapter 1). WCL analysis was limited to the detection and quantification of only nine ions: Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , and $\text{NO}_3^-/\text{ClO}_4^-$. Though a less thorough method of analyzing for soluble ions, the WCL analysis was performed on a subset of soils from the MDV in order to provide a complimentary analysis technique to create a catalog of WCL responses to a variety of Mars analog soils. A discussion of the WCL results is presented followed by a comparison of the IC and WCL data.

Ion Chromatography and Acid-Base Titration Results: Analysis of soils from all eleven pits by ion chromatography revealed the presence of five different cations: Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} and five different anions: Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , and ClO_4^- . ClO_4^- is discussed in detail in Chapter 3. Five ionic species, Na^+ , K^+ , Ca^{2+} , Cl^- , and SO_4^{2-} , were present in all samples, while NO_3^- was not detected in one sample, Mg^{2+} was not detected in two samples, and NH_4^+ was not detected in three samples indicating if these ions were present in the leachate they were at levels below the detection limits of the instrument. Additionally, while PO_4^{3-} was detected in all soils analyzed, only 7 of the 11 pits were analyzed for phosphate (soils in the stable upland zone were not analyzed for phosphate). Analysis of soils from all eleven pits by acid-base titration revealed carbonate was present in at least some of the soil horizons in the pits dug in the coastal thaw and inland mixed zones. However, there was no carbonate found in any soils from the stable upland zone. Bicarbonate was found in all soil horizons of all pits. Tables listing the concentration of each soluble ion in each soil leachate solution (in μM

and/or mM) and original soil sample (in $\mu\text{g}/\text{kg}$ and/or mg/kg) can be found in Appendix D.

The soluble ions detected in these MDV soil samples by ion chromatography and acid-base titration are similar to the ions that have previously been detected in the MDV. [35, 36, 37, 38] For the most part, all of the ions appear to be present in all soil horizons within each of the 11 pits. However, the salt composition varies greatly depending on the location of each pit and its corresponding elevation and climate conditions. Therefore, the following discussion of the soil profiles of soluble ions in the each of the 11 pits will be divided by microclimate zone.

Coastal Thaw Zone: A total of 23 soil samples from Taylor Valley collected from four different pits (Pits 1, 2, 3, and 4) dug at three different elevations were analyzed by IC and acid-base titration for soluble ion content. Pits 1 and 2 were dug at the same elevation ($21 \text{ m} \pm 5.5 \text{ m}$), with Pit 1 being dug in the trough of a polygon and Pit 2 being dug in the polygon's center. Pits 4 and 3 were dug at increasingly higher elevations ($41 \text{ m} \pm 4.9 \text{ m}$ and $108 \text{ m} \pm 5.5 \text{ m}$, respectively).

All four pits in Taylor Valley were dominated by the anion chloride. This is the result of the proximity of the coast and the influence of marine aerosols bringing in NaCl from the ocean into this valley. The next most abundant anion was sulfate. It has been suggested that the source of sulfate is also from marine aerosols. [35] Nitrate was the third most abundant anion in the Taylor Valley soils. Unlike Cl^- and SO_4^{2-} , NO_3^- does not originate from the ocean but is atmospheric in origin. The presence of nitrates in the MDV come from deposits on the polar plateau that are distributed throughout the valleys by the katabatic winds. The lower concentration of NO_3^- seen in

the coastal thaw zone is due to the high solubility of nitrates. Higher water activity in this zone results in the nitrates begin transferred through the soil and eventually out to sea. [4] Carbonate and bicarbonate were also present in the soils of Taylor Valley. Carbonates are present in this region mainly as the result of rock weathering of local rock material. Keys and Williams [48] have previously reported the presence of carbonates and bicarbonates in Taylor Valley as well as Wright Valley. Finally, the soils in Taylor Valley were also found to contain phosphate. The presence of phosphate is an indicator of biological processes. [48] In the warmer, wetter conditions of the coastal thaw zone, with the presence of small streams and even lakes that are inhabited with bacteria, it is not surprising to find phosphate in this microclimate zone.

The dominant cation in soils from Taylor Valley was sodium. Sodium correlates well with chloride as expected from the influx of NaCl from the ocean. Sodium could also be contributed from the ocean in the form of Na₂SO₄. Potassium, calcium and magnesium were also present in the soils of Taylor Valley. All three of these ions are known to accumulate in the Dry Valleys due to weathering. [35] There was also a small contribution of NH₄⁺ to the soils.

Figures 13, 14, 15 and 16 show the soil profiles for Pits 1, 2, 4, and 3, respectively. These soil profiles were created by plotting the concentration of each ion in the soil (in mg/kg) as a function of soil depth (in cm). Pit 2 (Figure 14) was dug at the same elevation as Pit 1 (Figure 13) and was part of the same polygon but the two pits exhibit very different soil profiles. The depth to the ice-table was 28 cm for both pits. Pit 2 which was dug in the middle of the polygon had seven distinct soil horizons above the permafrost while Pit 1 which was dug in the trench of the same polygon had only four distinct soil horizons above the permafrost. In addition to the increased number of soil horizons in Pit 2, the highest concentration of soluble ions was located at a

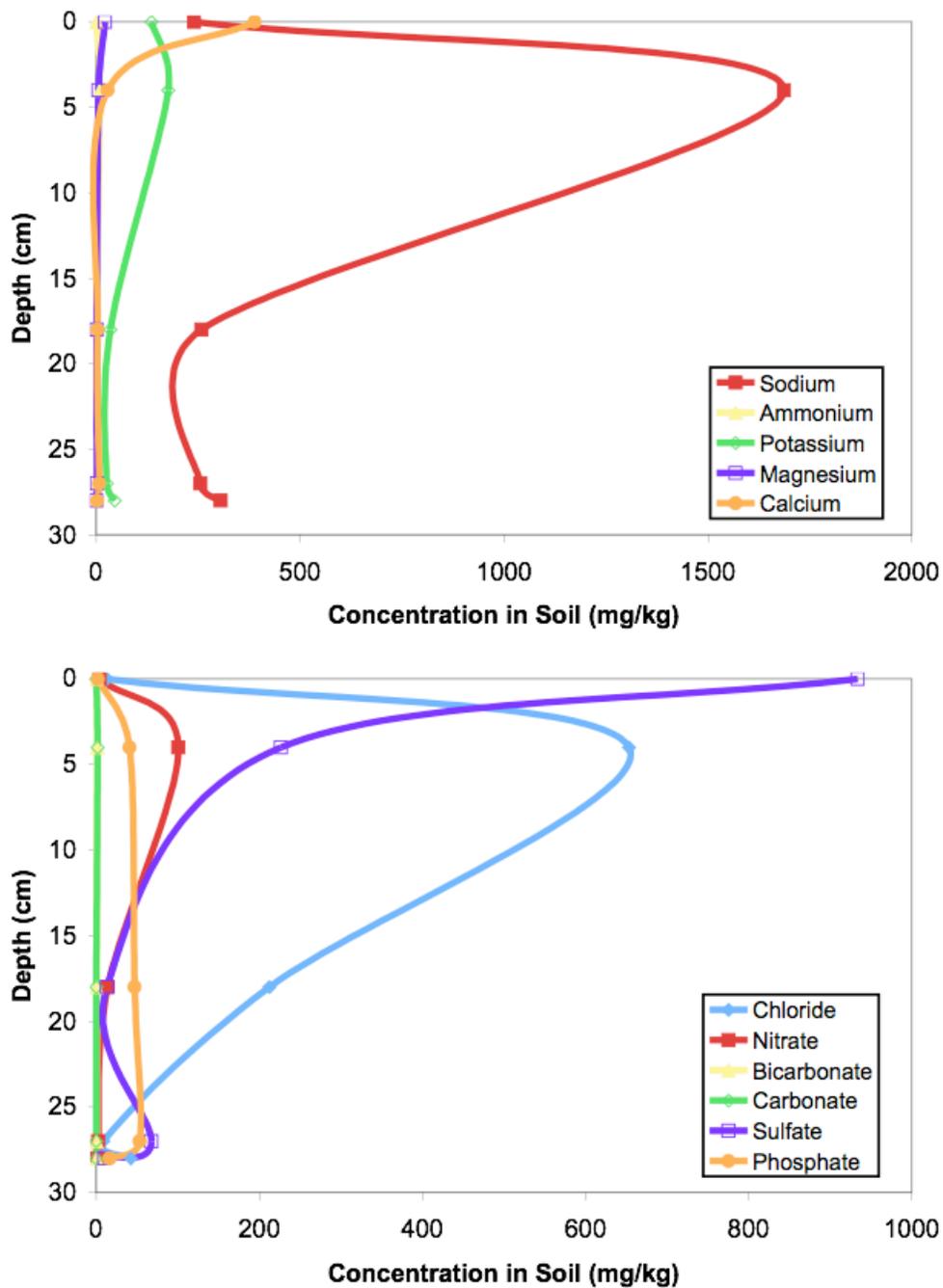


Figure 13: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of Taylor Valley Pit 1 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

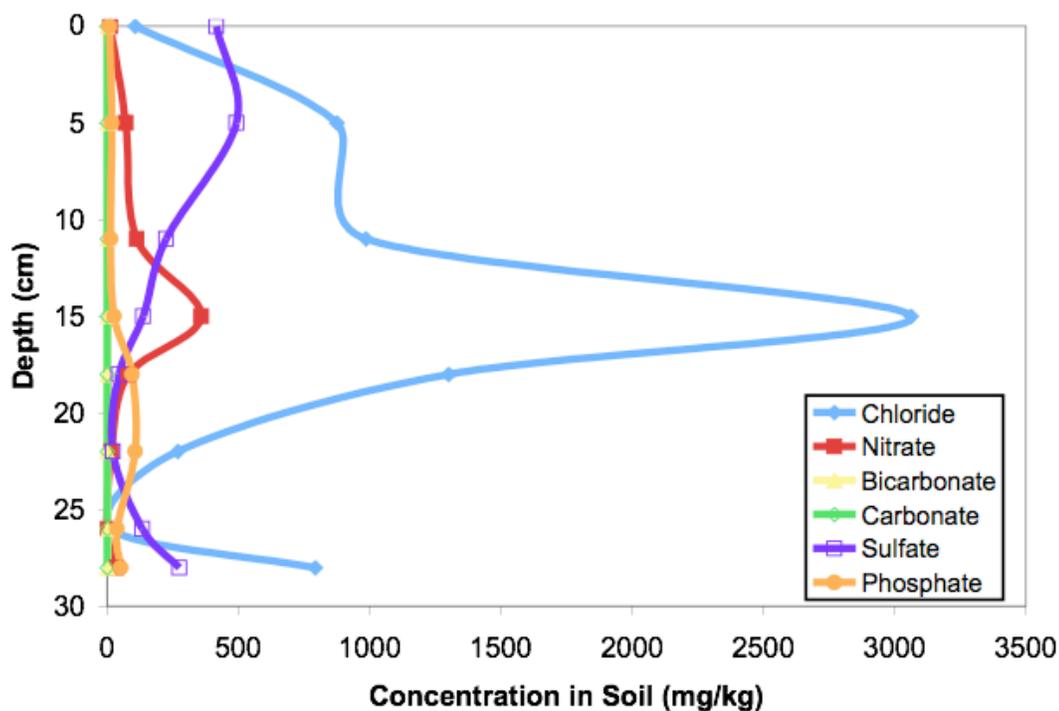
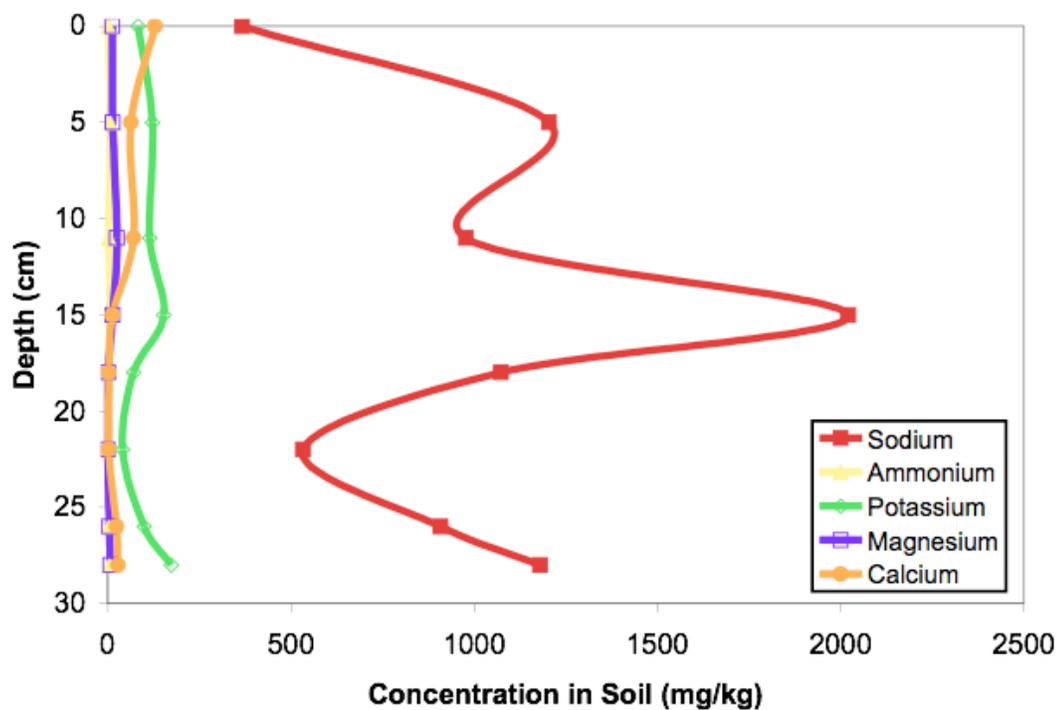


Figure 14: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of Taylor Valley Pit 2 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

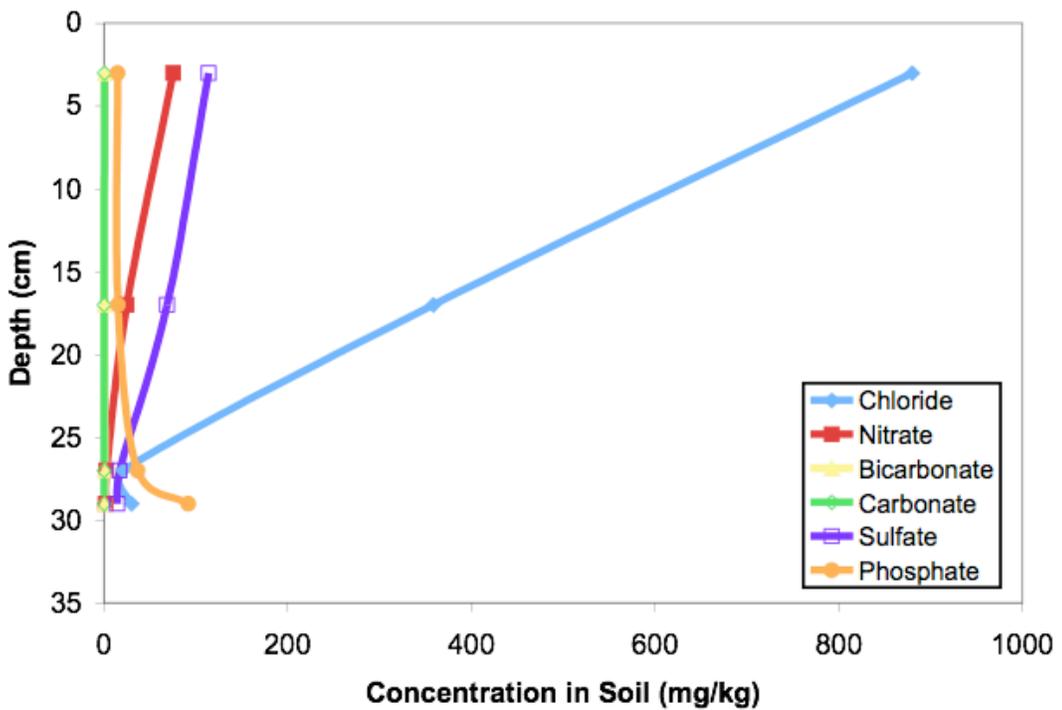
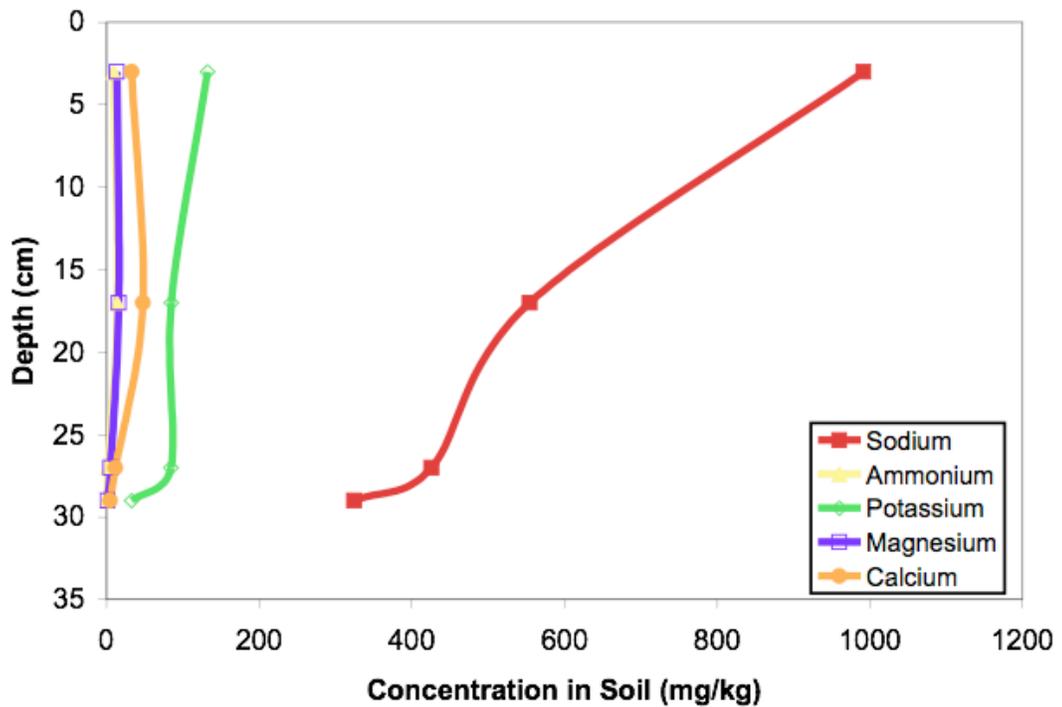


Figure 15: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of Taylor Valley Pit 4 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

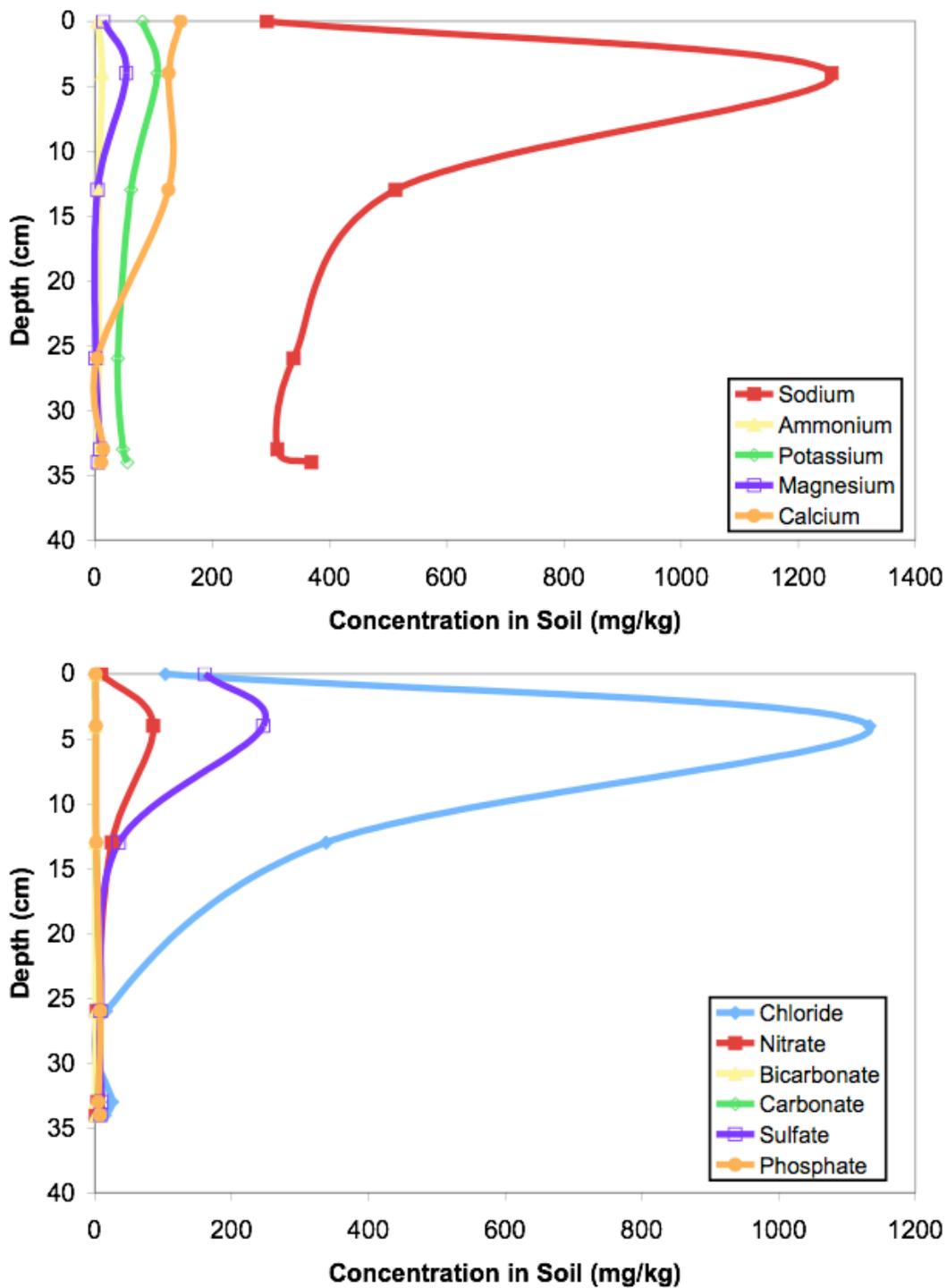


Figure 16: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of Taylor Valley Pit 3 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

depth of 15 cm, roughly half way to the permafrost while Pit 1 had the highest concentration of soluble ions in the first soil horizon below the pavement level at a depth of only four cm. The difference between these two soil profiles may be explained by the expansion and contraction of the soil which forms these polygonal shapes and accompanying troughs. This movement would disrupt the soil horizons, thus changing the soil profile in the trough.

The soil profiles for Pits 3 and 4 were similar to Pit 1. No record was made as to whether these pits were dug in an area of patterned ground and if so in the middle or trough of a polygon. The highest concentration of soluble ions were located in the first soil horizon below the pavement level, at either 3 cm (Pit 4) or 4 cm (Pits 1 and 3) in depth. This high ion concentration lies between 10-15% of the depth to the ice-cemented soil layer in each pit. The trend for these three pits is an overall decrease in soluble ion content with depth from the soil horizon directly below the pavement. A soil sample from the pavement level was analyzed for Pits 1 and 3 and the overall content of soluble ions was low in comparison to the first soil profile. The pavement level from Pit 4 was not analyzed due to insufficient sample material, however, it can be assumed the results would be similar to those seen in Pits 1 and 3.

Overall, the results from the analysis of four pits in the coastal thaw zone, specifically Taylor Valley, presented herein were in good agreement with the previously analyzed soils from this region. [36, 37, 38] As expected, the soils in this zone were dominated with Na^+ , Cl^- , and SO_4^{2-} due to this valley's proximity to the coast. Likewise these soils had an abundance of K^+ , Ca^{2+} , and Mg^{2+} from the high level of rock weathering as a result of this zone's increased moisture content.

Inland Mixed Zone: Soils were collected from Victoria and Wright Valleys in the inland mixed zone. Two pits (Pits 8 and 9) were dug in Victoria Valley and a total of eight soil samples were analyzed, four soil horizons from each pit. Only one pit was dug in Wright Valley (Pit 13) and only three soil horizons were collected and analyzed.

Due to the limitation in sample size from this zone (only 11 soil horizons were collected and analyzed, no more than four per pit and no pavement samples), it was much more difficult to determine with confidence any trends for this data. All of the anions and cations found in the soil samples from the coastal thaw zone were also present in the inland mixed zone. As in the coastal thaw zone, the soils from the inland mixed zone were also dominated with Cl^- , SO_4^{2-} and Na^+ . Both Cl^- and SO_4^{2-} correlate well with Na^+ and suggest parent salts of NaCl and Na_2SO_4 which both have a marine origin. [35] As in the coastal thaw zone, NO_3^- was the next most abundant anion after Cl^- and SO_4^{2-} that like in the coastal thaw zone came from deposits on the polar plateau distributed by the katabatic winds. [35] Again, the high solubility of nitrates resulted in most of this ion being transported out of the soil, but the greater aridity of this climate zone can account for the higher NO_3^- concentration in the inland mixed zone compared the coastal thaw zone. Lower concentrations of HCO_3^- , CO_3^{2-} and PO_4^{3-} were also present in the zone from the same sources which result in these ions in the coastal thaw zone. The next most abundant cation, after Na^+ , present in the inland mixed zone is Ca^{2+} , followed by Mg^{2+} and K^+ which are known to accumulate in the Dry Valleys due to weathering. [35] As in the coastal thaw zone, there was also a small contribution of NH_4^+ in the soil.

Figures 17, 18, and 19 show the soil profiles for Pits 8, 9, and 13, respectively. These soil profiles were created by plotting the concentration of each

ion in the soil (in mg/kg) as a function of soil depth (in cm). The soil profiles for Pit 9 in Victoria Valley and Pit 13 in Wright Valley were similar. The highest concentration of soluble ions was present in the first soil horizon under the pavement level (at a depth of 2 cm in Pit 9 and 4 cm in Pit 13). Pavement samples were not analyzed for any pits in the inland mixed zone due to insufficient sample material. The overall trend in each of these pits was a decrease in both anions and cations with depth. The depth to the permafrost layer measured 19 cm, 27 cm, and 23 cm in Pits 8, 9, and 13, respectively. This was much shallower than the 35-70 m permafrost depths previously seen in this zone. [35] In addition to the shallow permafrost layer there were also fewer soil horizons before reaching the permafrost layer than in the coastal thaw zone, with four each in Pits 8 and 9 and only three in Pit 13. Due to the limited number of soil horizons, very few soils were collected and analyzed in this zone. Therefore, it was difficult to discover much about the soils from the inland mixed zone.

Overall, the results from the limited analysis of soils collected from the inland mixed zone were in agreement with previously analyzed soils from this region. [36, 37, 38] Most of the investigations of the inland mixed zone have focused on soils collected from Wright Valley, presumably due to its lower elevation and closer proximity to McMurdo Station. J.G. Bockheim [49] listed the order of concentration of both anions and cations in Wright Valley similar to what was seen in these pits. Gibson et al. [32] also listed a similar list of soluble ions in Wright Valley and was in agreement that the concentration of these ions decrease with soil depth. Keys et al. [48] and Green et al. [50] discussed the presence of PO_4^{3-} in the soil in Wright Valley as well as either CO_3^{2-} or HCO_3^- . As expected, the soils contained the same anions and cations as those in the coastal thaw zone, however, the concentrations of

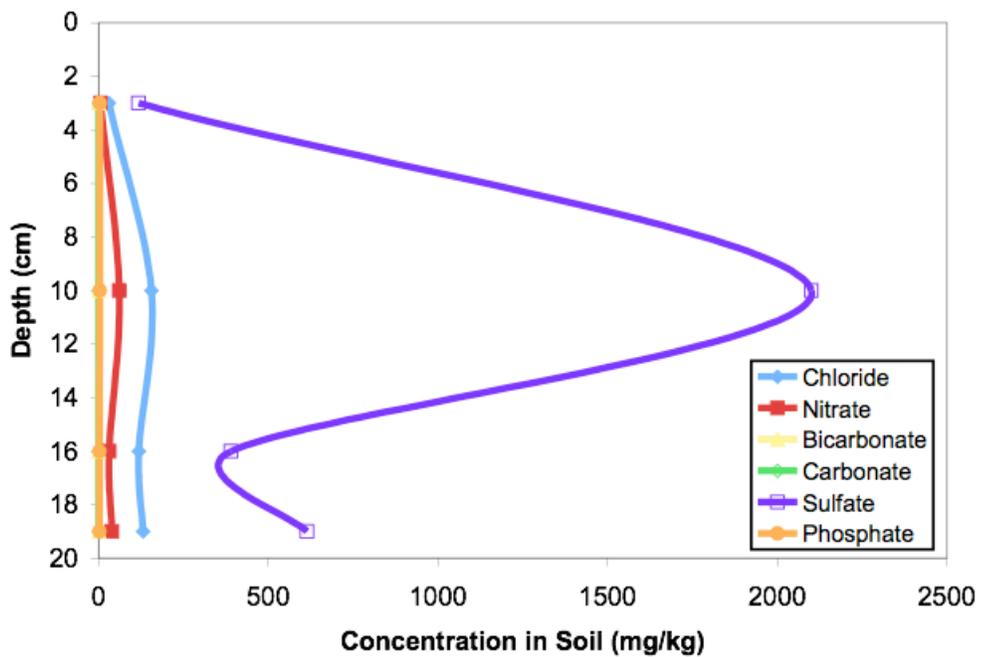
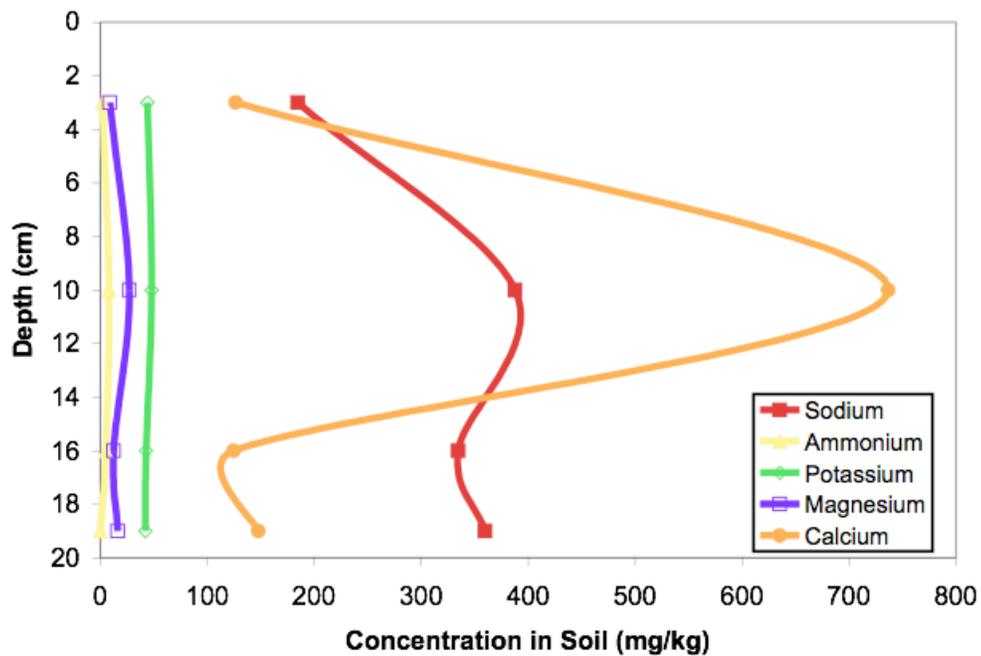


Figure 17: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of Victoria Valley Pit 8 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

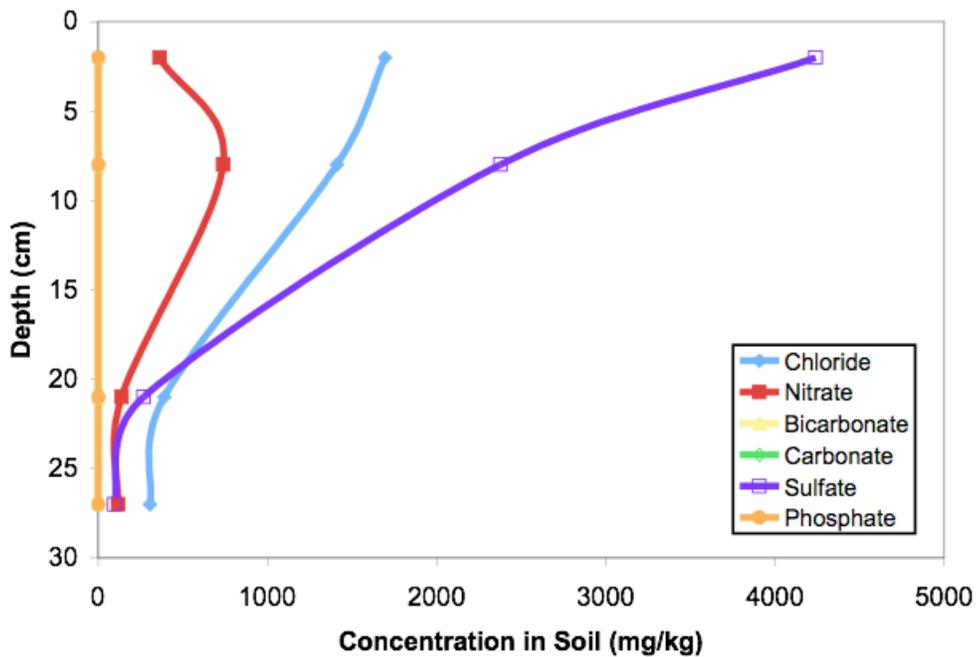
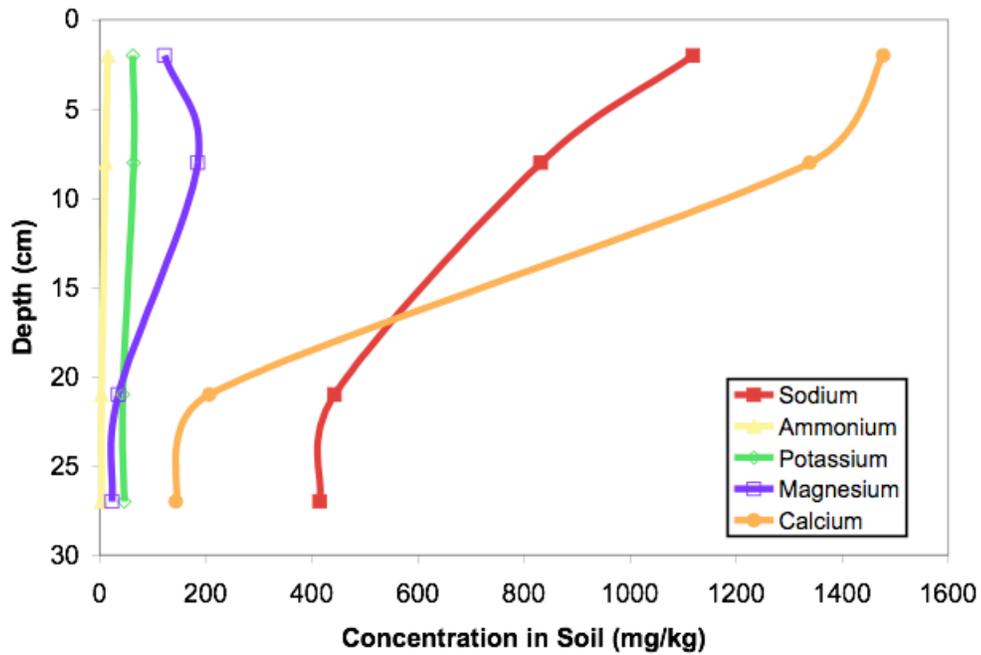


Figure 18: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of Victoria Valley Pit 9 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

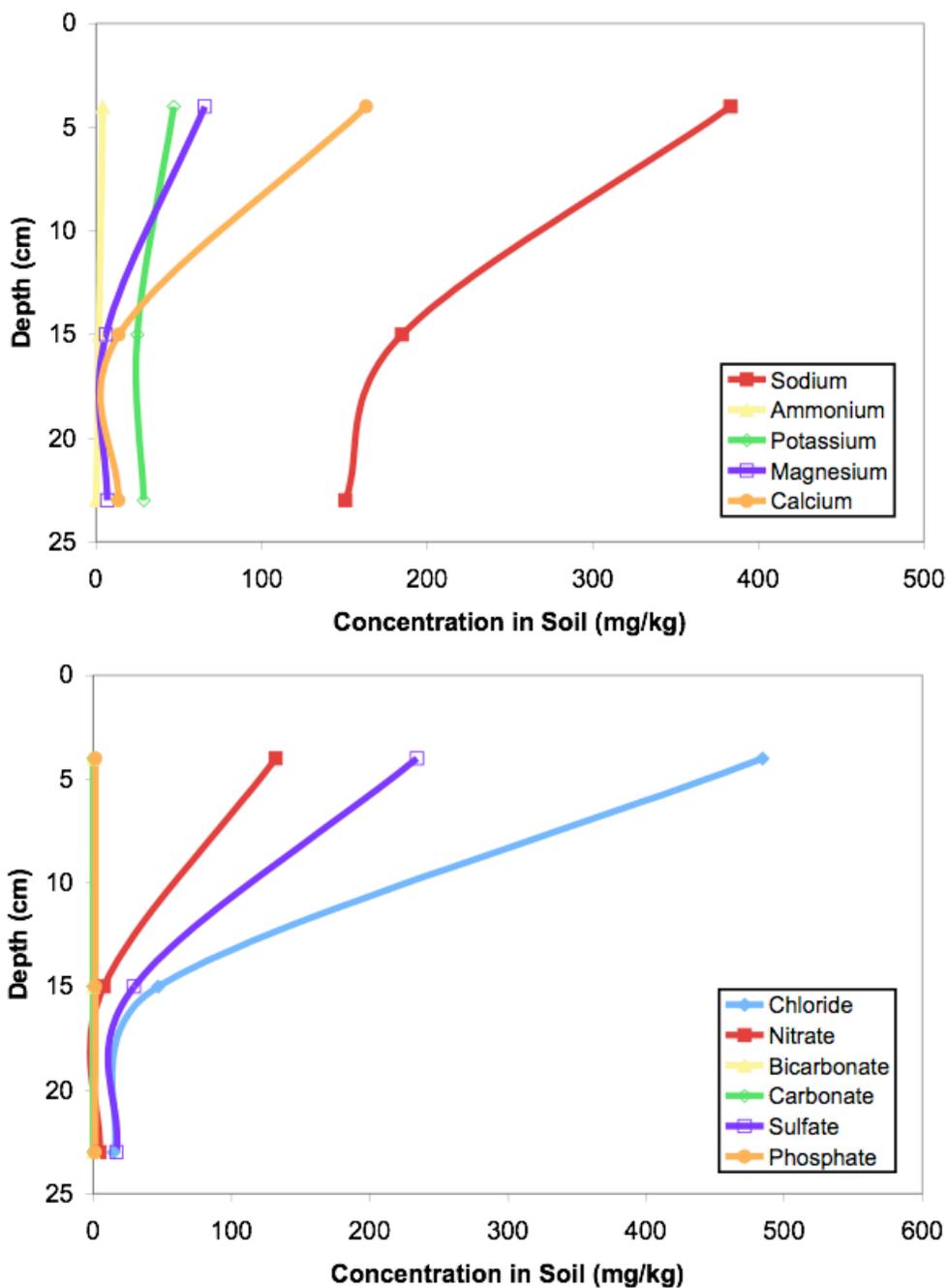


Figure 19: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of Wright Valley Pit 13 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

the most soluble species, such as nitrate, were found in higher concentrations in this zone due to the increased aridity and decreased annual precipitation.

Stable Upland Zone: Soil were collected from Beacon and University Valleys in the stable upland zone. Two pits (Pits 7 and 10) were dug in University Valley and a total of nine soil samples were analyzed, four soil horizons in Pit 7 and five in Pit 10. Two pits (Pits 11 and 20) were dug in Beacon Valley. Four soil horizons were analyzed in Pit 11. In Pit 20, a total of 15 samples were analyzed, seven samples were soil and the other eight were dried permafrost.

Unlike the coastal thaw zone and the inland mixed zone, there was no carbonate present in the soils analyzed from the stable upland zone. (It is not certain whether or not phosphate was present because it was not analyzed for in these soils, however, given the rarity of possible life in this zone and phosphate's presence being a indicator of biological processes, it is unlikely that phosphate would be found in this zone.) However, the upper stable zone soils do contain the other anions and cations present in the other two microclimate zones.

Soluble ions in Beacon Valley were dominated by the anions Cl^- and SO_4^{2-} and the cations Ca^{2+} and Na^+ . Calcium and sulfate correlated well in both pits as did sodium and chloride, suggesting parent salts of CaSO_4 and NaCl . These same correlations were seen in the inland mixed zone. The NaCl , in the form of halite, in this high elevation valley does not come from marine aerosols but rather snowfall off the polar plateau. [35] The CaSO_4 could be in either the mineral form anhydrite (CaSO_4) or gypsum ($\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$). Gypsum was detected by XRD in the soil from the stable upland zone, specifically all soil horizons in University Valley Pit 7. [4] Due to the hyper-aridity and lack of

wetting/hydration in this zone, there was the possibility that CaSO_4 was in the mineral form anhydrite as well. Nitrate was the third most abundant anion in this valley. This concentration was higher than what was seen in the coastal thaw or inland mixed zone. The additional NO_3^- can be attributed to the proximity of this valley to the polar plateau where snowfall brings an influx of HNO_3 or NaNO_3 and the higher aridity which keeps this soluble species from being washed away. NH_4^+ was also present in this valley at concentrations higher than in the other two microclimate zones. The presence of ammonium, like nitrate, was also most likely from snowfall off the polar plateau in the form of $(\text{NH}_4)_2\text{SO}_4$. Likewise, Mg^{2+} , K^+ and HCO_3^- were also present in this valley presumably from rock weathering. [35]

University Valley was dominated by SO_4^{2-} and Ca^{2+} and the two correlated well suggesting the parent salt of CaSO_4 , again in the mineral form of either anhydrite (CaSO_4) or gypsum ($\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$). Gypsum was detected in all soil horizons of Pit 7 by XRD. [4] The next most abundant ions are Na^+ and NO_3^- . These ions also correlate well suggesting a parent salt of nitratine (NaNO_3), the source of which was snowfall from the polar plateau. Like gypsum, nitratine was also detected in all soil horizons of Pit 7 by XRD. [4] The abundance of Cl^- was lower in this valley than in Beacon Valley suggesting there was less influx of NaCl in this valley than in neighboring Beacon Valley. Mg^{2+} , K^+ , NH_4^+ and HCO_3^- were also all present in University Valley as the result of rock weathering (Mg^{2+} , K^+ , and HCO_3^-) and snowfall from the polar plateau (NH_4^+). [35]

Figures 20, 21, 22 and 23 show the soil profiles for each pit in both Beacon and University Valleys. These profiles were created by plotting the concentration of each ion in the soil (in mg/kg) as a function of depth (in cm). The soil profiles for the two pits dug in Beacon Valley were similar with the maximum

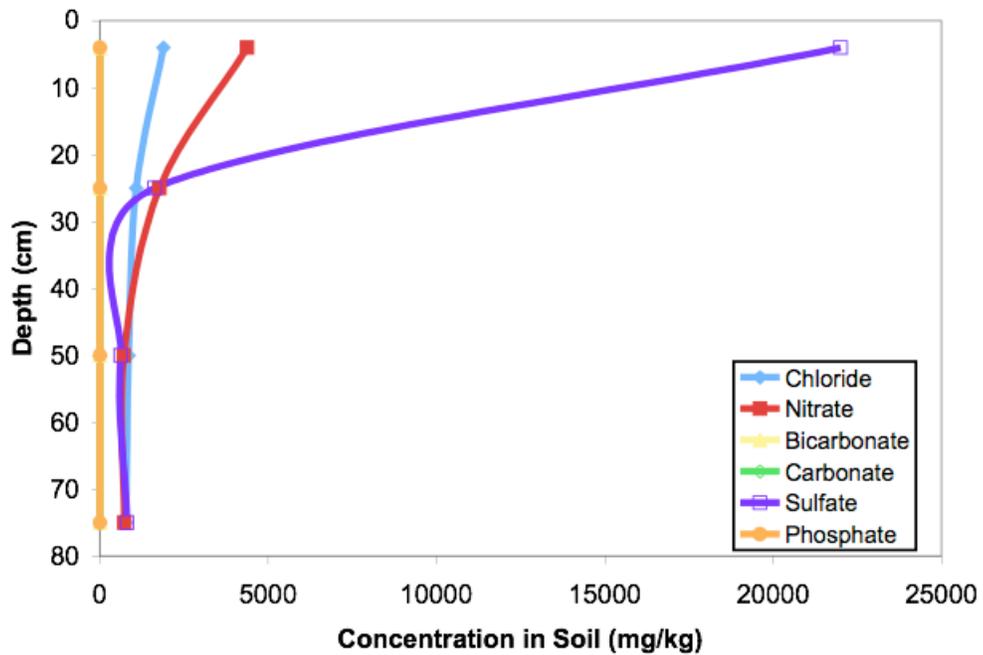
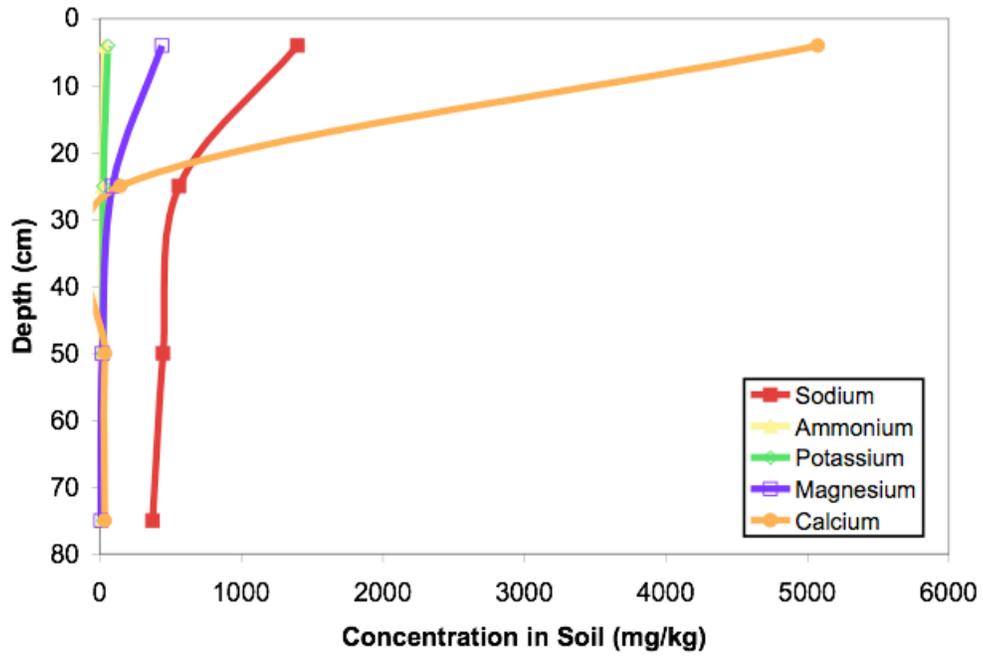


Figure 20: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of Beacon Valley Pit 11 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

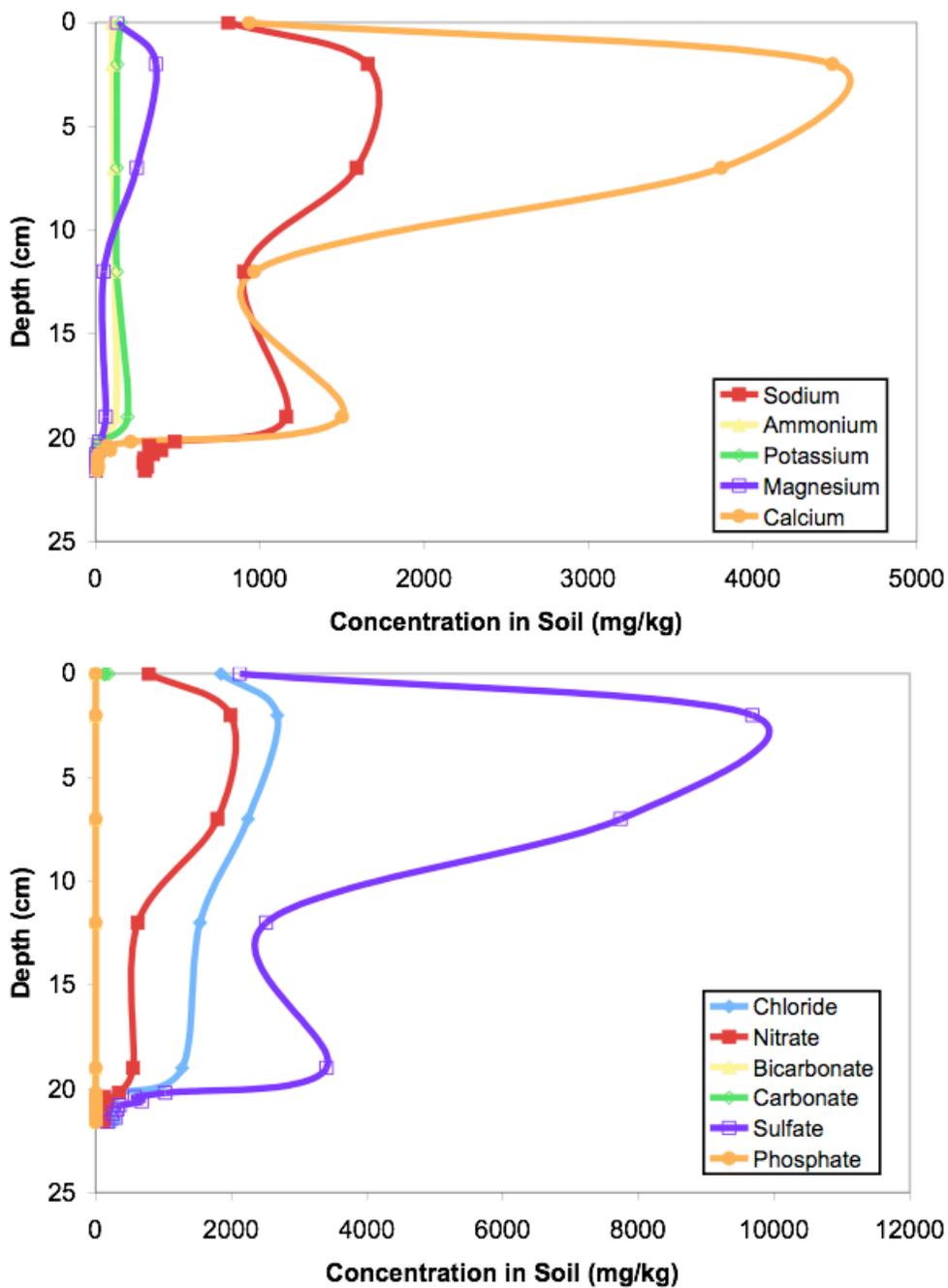


Figure 21: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of Beacon Valley Pit 20 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

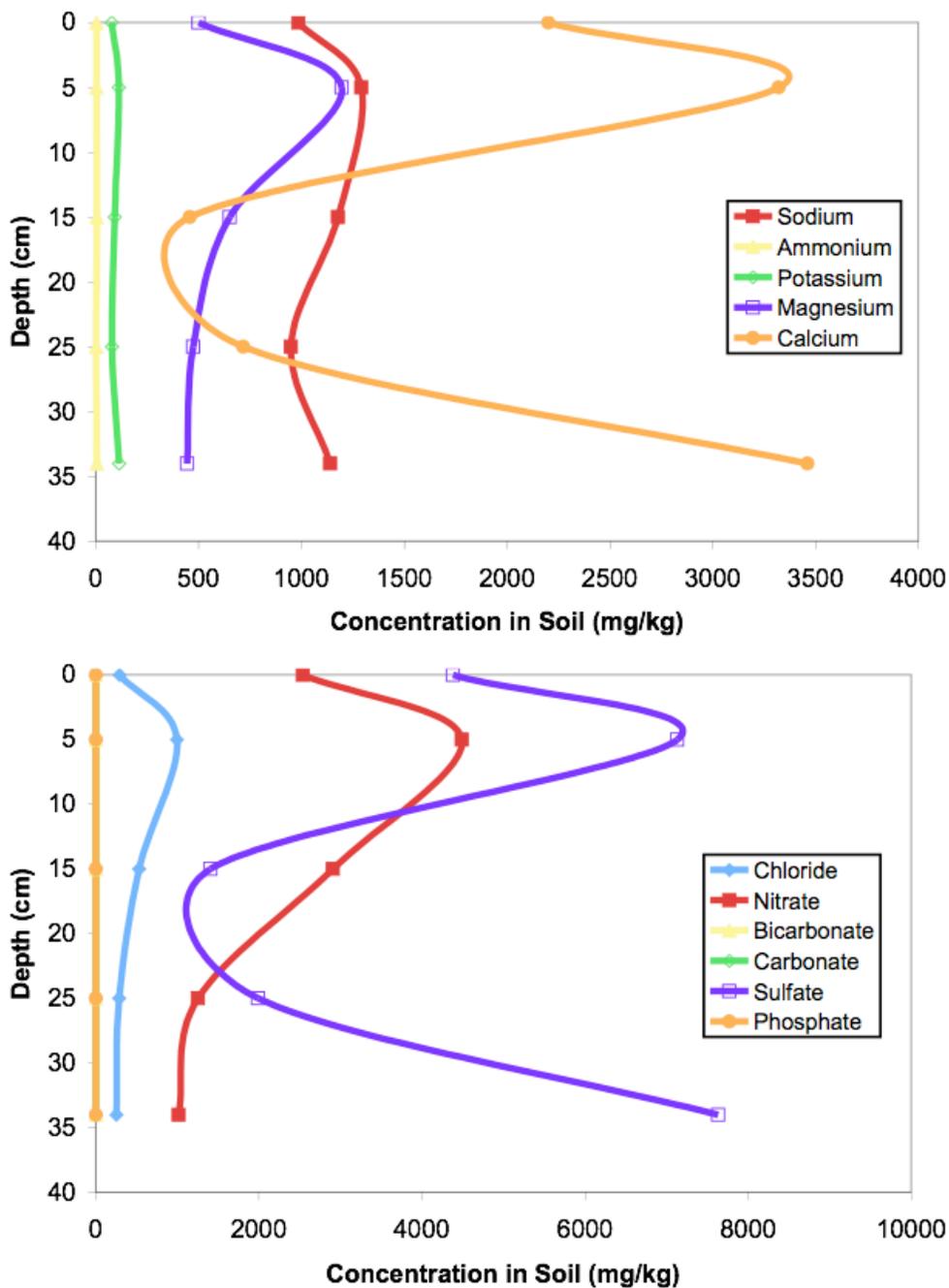


Figure 22: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of University Valley Pit 7 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

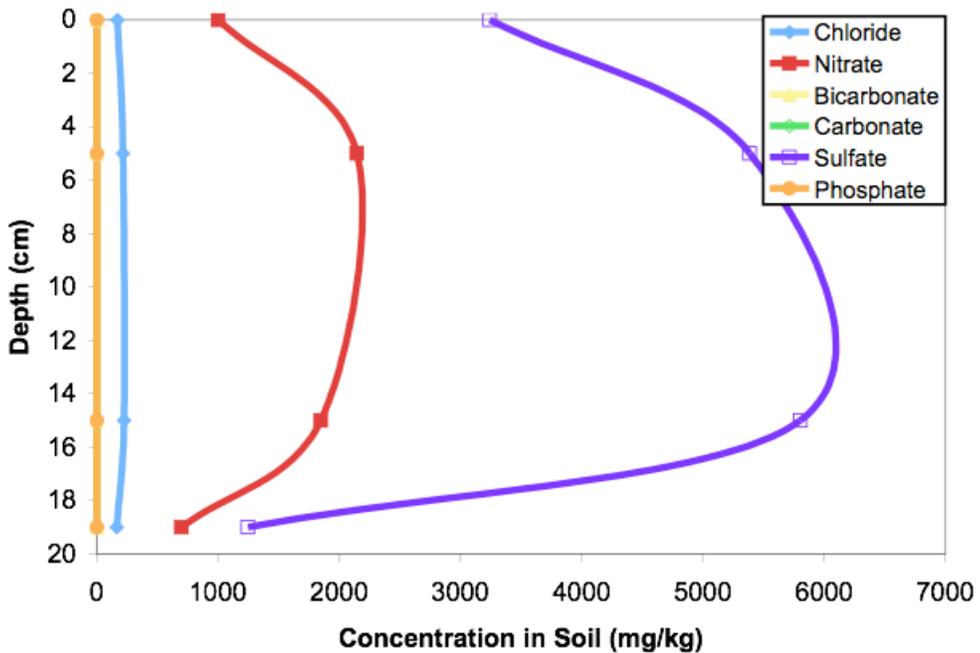
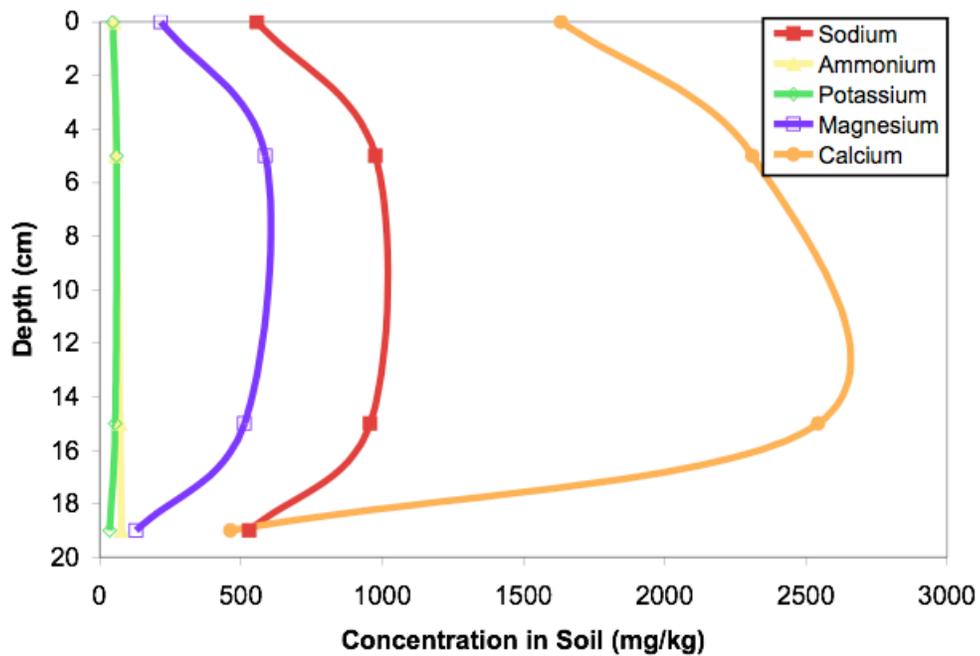


Figure 23: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when 1 gram of University Valley Pit 10 soil was leached in 25 mL of 18.2mΩ water for ~24 hours and analyzed by IC and acid-base titration, as a function of depth (in cm)

concentration of ions present in the first soil horizon below the pavement level. The concentration of ions then decreased with depth. This type of profile, with maximum ion concentration directly under the pavement and decreasing ion content with depth, was also seen in Pits 1, 3, and 4 in Taylor Valley, Pit 13 in Wright Valley and Pit 9 in Victoria Valley. One interesting difference between the soil profiles of Pits 11 and 20 was the difference in depth to the permafrost layer. In Pit 20, the permafrost layer was 20 cm deep, but in Pit 11 the pit was dug 105 cm deep and still no permafrost layer was found. Looking at the extended soil profile of Pit 20 dug an additional 1.6 cm into the permafrost and samples collected every 0.2 cm, the overall concentration of ions present were low (≤ 2.2 mM total in the soil leachate or ≤ 2440 mg/kg total in the soil in each sample analyzed) and relatively consistent throughout.

The soil profiles from the two pits dug in University Valley (Figures 22 and 23) were different from those in Beacon Valley (Figures 20 and 21). In Pit 7, the soil horizon with maximum ion concentration was again directly below the pavement level and then the concentration of ions began to decrease. However, there was a sharp rise to high ion concentration seen again at the permafrost layer at a depth of 34 cm. The profile of Pit 10 was different than the profile for Pit 7, with an increase in ion content from the pavement to first soil horizon with remained high down to a depth of 15 cm before decreasing in concentration to the permafrost layer at 19 cm deep.

Overall, the soils from the stable upland zone were dominated by Ca^{2+} and SO_4^{2-} with large contributions from Na^+ , Cl^- , and NO_3^- . The major contributors to the salts present in the zone were snowfall from the polar plateau and rock weathering. This zone had the highest salt concentration due to the high aridity, which allowed salts to accumulate and concentrate in the soils. There are few references to soils analyzed from this microclimate

zone and those focus more on soils from Beacon and Arena Valley. [38, 39, 41] This zone has been less studied than the others due to its challenging location.

Wet Chemistry Laboratory Results: The WCL is only capable of detecting and quantifying eight ions, Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , and NO_3^- or ClO_4^- . It is known from the IC analysis that the ratio of $\text{NO}_3^-:\text{ClO}_4^-$ in soils where ClO_4^- was detected was large, ranging from a low of 12.5:1 in the coastal thaw zone to as high as 7600:1 in the stable upland zone. Due to the large $\text{NO}_3^-:\text{ClO}_4^-$ in the MDV soils studied by IC and selectivity of the $\text{NO}_3^-:\text{ClO}_4^-$ electrode, this electrode was considered to be a NO_3^- ISE for these samples. Due to the limitations of the number of different soluble ions detectable by WCL only a subset of the MDV soil samples were analyzed: Pits 1 and 2 from Taylor Valley and Pits 7 and 10 from University Valley.

Of the eight ions detectable by WCL only Na^+ , NH_4^+ , and K^+ were detected at measurable quantities in all soil horizons in all four pits. The ions, Mg^{2+} , Ca^{2+} , Cl^- and NO_3^- were detected in all soils horizons from Pits 7 and 10 in University Valley, while in Taylor Valley Pits 1 and 2 they were present in measurable quantities in only some of the soils horizons. Additionally, Ba^{2+} was also found in measurable quantities in one soil horizon in Pit 1, three soil horizons in Pit 7 and all four soil horizons in Pit 10.

Tables listing the concentration of each soluble ion in each soil sample detected and quantified by WCL can be found in Appendix E. In compiling the data from the WCL analysis, there were some similarities to the results from the IC analysis discussed above. However, there was also some noticeable differences. A comparison of the data collected from these two complimentary soluble ion analysis techniques is presented along with a justification of the variations in these results.

Comparison of WCL and IC Soluble Ion Results: In comparing the IC data (Appendix D) to the WCL data (Appendix E) it was seen that WCL reported a greater number of soils with ions below the instruments limit of detection. Of the 22 soils analyzed, eight fell below the limit of detection of Mg^{2+} by the WCL as compared to only two in the IC. Six of the 22 soils fell below the limit of detection of NO_3^- in WCL as compared to only one in the IC and 15 fell below the limit of detection of Ba^{2+} in WCL as compared to 13 in the IC. In addition, all 22 samples had detectable levels of Ca^{2+} and Cl^- measured by the IC, however, there were six soils below the limit of detection for Ca^{2+} and two for Cl^- in the WCL.

In calculating the limits of detection for both instruments it was shown that the limit of detection of all eight ions being compared were lower in the IC than in the WCL. It is for this reason the IC was able to detect Mg^{2+} , Ca^{2+} , Ba^{2+} , NO_3^- , and Cl^- in soil samples where these ions were not detected by WCL. No Ba^{2+} was detected in Pit 10 by the IC because these soil leachates were diluted an additional 100-fold prior to analysis causing the already small quantity of Ba^{2+} to fall below the instrument's limit of detection for this ion.

In addition to the difference in detection limits of the two instruments resulting in low concentrations of some ions go undetected by the WCL there was also a discrepancy in the concentrations of some ions at values far exceeding the instruments' detection limits. Ideally, analysis by two complimentary analysis techniques for soluble ions should generate, within reasonable error, the same concentration of ions present in the same soil sample. Comparison of the IC and WCL data shows that for some ions there was a significant difference in the concentration determined by these two techniques. Most noticeably, the concentration of Na^+ determined by IC was one to two orders of magnitude greater in samples from Pits 1, 2, and 7 than the corresponding

concentration determined by WCL. Most of the soils in Pit 7 also showed an order of magnitude greater concentration of K^+ , Mg^{2+} , Ca^{2+} , Cl^- , and NO_3^- in the IC data over the WCL data while only NH_4^+ in Pit 10 was an order of magnitude greater in concentration calculated by the IC.

Despite the various discrepancies in the concentration of ions quantified by each method there were some similarities in the soil profiles for Pits 1, 2, and 7 when plotting the concentration of each ion in the soil (in mg/kg) for each method as a function of soil depth (in cm). While the concentrations may have differed between the two methods of analysis, the trend of most ions down the pit was similar. Only Na^+ in Pit 1, NO_3^- , in Pit 2 and Mg^{2+} in Pit 7, showed a considerable variation in depth profile between the two methods. However, in Pit 10 the depth profiles differed for all ions between the two methods. The soil profiles for Pit 10 created from the IC data showed a higher concentration of Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , and NO_3^- at depths of 5 and 15 cm with lower concentrations at depths of 0 and 19 cm (Figure 23), while the soil profiles created from the WCL data showed a higher concentration of Mg^{2+} only at a depth of 5 cm and a higher concentration of Na^+ , Ca^{2+} , Cl^- , and NO_3^- only at a depth of 15 cm.

Comparison of the ion-to-ion concentration ratios calculated from both the WCL and IC data (in mg/kg in the soil) showed little similarity. Of the 21 possible combination of ion-to-ion concentration ratios for Pit 1 only 2 ion-to-ion ratios were the same when calculated from both WCL and IC data: $[Mg^{2+}]:[NH_4^+]$ and $[Ca^{2+}]:[K^+]$. Two combinations were also equivalent in Pit 2: $[Ca^{2+}]:[K^+]$ and $[Ca^{2+}]:[Mg^{2+}]$, while three combinations were equivalent in Pits 7 and 10: $[Ca^{2+}]:[Mg^{2+}]$, $[Mg^{2+}]:[Cl^-]$, and $[Mg^{2+}]:[NO_3^-]$ in Pit 7, and $[Na^+]:[NO_3^-]$, $[Ca^{2+}]:[Mg^{2+}]$, $[Ca^{2+}]:[NO_3^-]$ in Pit 10.

Variations in ion-to-ion ratios and ion trends down soil profiles, along with

differences in ion concentrations as large as two orders of magnitude, suggest one or both of these two complimentary techniques, IC and/or WCL, was not providing accurate analysis of the soluble ions in the McMurdo Dry Valley soils. Some of the discrepancy in the data produced from these techniques can be attributed to working with natural and complex samples. The soils, while crushed to a particle size of >600 microns prior to analysis, were not necessarily homogeneous and since different soil aliquots were used for each analysis technique some of the variation in the results can be attributed to the sample's heterogeneity.

Another reason for the discrepancy between the two techniques comes for the reliability of the instrument. With ion chromatography, proper care and regular maintenance of the instrument, including replacement of the separation column, eluent generator cartridge and suppressor ensures reliable data analysis. However, the WCL testbeds and flight units were specially designed for the Phoenix mission and contain an array of solid pellet crystal and PVC membrane ISEs (see Table 1) susceptible not only to fouling but also to losing their selectivity overtime if not properly maintained. The WCL testbeds have been regularly used for testing over the span of more than five years, a considerably long lifetime for these electrodes.

Fouling of a single or even multiple electrodes within the WCL would be rather evident upon calibration. However, the loss of an ISEs selectivity would be more difficult to discover unless regular selectivity tests were performed. Ideally, PVC membrane ISEs should be stored in solution containing only the ion of interest and a corresponding counter ion but because WCL was an array of different sensors within a single cell, it was not possible to store the individual ISEs in this manner. Instead, the cell was sealed with a small amount of water or TS20 solution inside to keep the ISEs hydrated during

storage. Less than ideal storage, along with multiple calibrations overtime with solutions containing ions for all the ISEs present in addition to numerous experimentation, even with solutions which were not considered dangerous to the ISEs (solutions known to foul certain sensors), it was possible that over time the ISEs became less selective. Loss of selectivity in the pair of lithium ISEs would be the most detrimental to the WCL's performance since the lithium ISEs were always used as the reference electrode and assumed to have a high selectivity over possible interfering ions such as Na^+ and K^+ . If, over time, Li^+ began to respond to Na^+ or other ions in addition to Li^+ , there would no longer be a stable reference potential when a sample was added to the TS21 solution.

A test was performed to measure a known quantity of NaCl in TB2 used for the analysis of the MDV soils. A known quantity of NaCl was added to the TS21 solution to result in an increase ~ 50 mM Na^+ and Cl^- . When the data was processed to subtract out the response of one of the Li^+ ISE, an increase of 43.5 mM of Na^+ and 42.2 mM Cl^- was measured, which was slightly less than the 45.5 mM Na^+ and 43.2 mM Cl^- measured by the IC. More interestingly, while NH_4^+ , Ba^{2+} , and NO_3^- all measured the same concentration in the TS21 solution with additional NaCl in solution as the TS21 solution, the concentration of K^+ , Mg^{2+} , and Ca^{2+} all decreased. Therefore, the Li^+ sensor was shown to have some selectivity to the added Na^+ , causing the Li^+ potential to increase upon sample addition and resulting in the measured decrease in K^+ , Mg^{2+} , and Ca^{2+} concentration. The lack of decrease in the NH_4^+ , Ba^{2+} , and NO_3^- can be attributed to the mV noise of these sensors causing the change in their mV response to go undetected. The analysis was repeated using the second Li^+ reference in TB2 and the same result was shown.

Thus, it was shown the Li^+ sensors in TB2 have become less selective over-

time and will respond to increases in Na^+ concentration. It is likely these electrodes will also respond to the other cations present in the test solutions: NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , and Ba^{2+} . The reference ISEs inability to be selective to Li^+ means any additional Na^+ or other cations in solution will increase the reference electrode's mV response, causing a greater mV response to be subtracted from each electrode's mV response and leading to a lower ion concentration calculated than is actually present in the sample. This explains the discrepancy between the higher concentration of ions detected in the IC and lower concentrations for the same sample detected in WCL.

There were several drawback encountered when analyzing the MDV soils for soluble ions by WCL. WCL was limited to only eight ions, which could be identified and quantified. The WCL also exhibited higher limits of detection for all ions compared to the IC resulting in instances where small quantities of ions in certain soils could not be detected. Finally, the reference Li^+ ISEs in WCL were found to be less selective than they once were, due to age and extended usage, resulting in lower ion concentrations detected. Due to the limitations encountered in running the WCL for the determination of soluble ions, the other soils from the MDV were not analyzed and only the IC data for soluble ions will be discussed when comparing the soils from the three microclimate zones in the MDV and the subsequent comparison of the MDV soils to the soil on Mars at the Phoenix Lander site.

2.4.2 Comparison of Ions in the Three Microclimate Zones

All three climate zones contained the same four anions: Cl^- , NO_3^- , HCO_3^- and SO_4^{2-} . Carbonate and phosphate were found only in the coastal thaw zone and inland mixed zone. However, soils in the stable upland zone were not analyzed for PO_4^{3-} . In the samples containing CO_3^{2-} and PO_4^{3-} , CO_3^{2-}

was always at a higher concentration than PO_4^{3-} .

Relative Abundance of Ions: Figure 24 (top) depicts the relative abundance of each anion in all 11 pits dug throughout the MDV. Carbonate, bicarbonate and phosphate were always in the lowest abundance in all 11 pits and were excluded from Figure 24. Chloride, nitrate and sulfate varied in abundance with increasing elevation. At the lowest elevations, all four pits in Taylor Valley (Pits 1, 2, 3, and 4) and the pit in Wright Valley (Pit 13) Cl^- dominated followed by SO_4^{2-} and then NO_3^- . The high abundance of Cl^- at these low elevations was due to the proximity to the coast where marine aerosols carried in high concentrations of Cl^- to deposit in the soils. Increasing higher in elevation, the two pits in Victoria Valley (Pits 8 and 9) SO_4^{2-} began to dominate over Cl^- and then NO_4^- as some of the marine influence was reduced. At the highest elevations, the two pits in University Valley (Pits 7 and 10) NO_3^- became the second most abundant anion after SO_4^{2-} and Cl^- fell to the third most abundant anion. The increased NO_3^- was the result of snowfall off the polar plateau present at these higher elevations.

All three microclimate zones contained the same five cations: Na^+ , K^+ , NH_4^+ , Mg^{2+} , and Ca^{2+} . However, as with the anions, the order of the concentration of these ions, from highest concentration to lowest concentration, changed with increasing elevation. Figure 24 (bottom) depicts the relative abundance of each cation in each of the 11 pits. In the coastal thaw zone and the inland mixed zone, all the pits were dominated with Na^+ coming in to this zone by marine aerosols. As the elevation increased to the stable upper zone, Ca^{2+} replaced Na^+ as the highest concentration cation. Ca^{2+} decreased with elevation from the highest concentration ion in the stable upper zone, the second highest in the inland mixed zone, and the third highest concentration ion

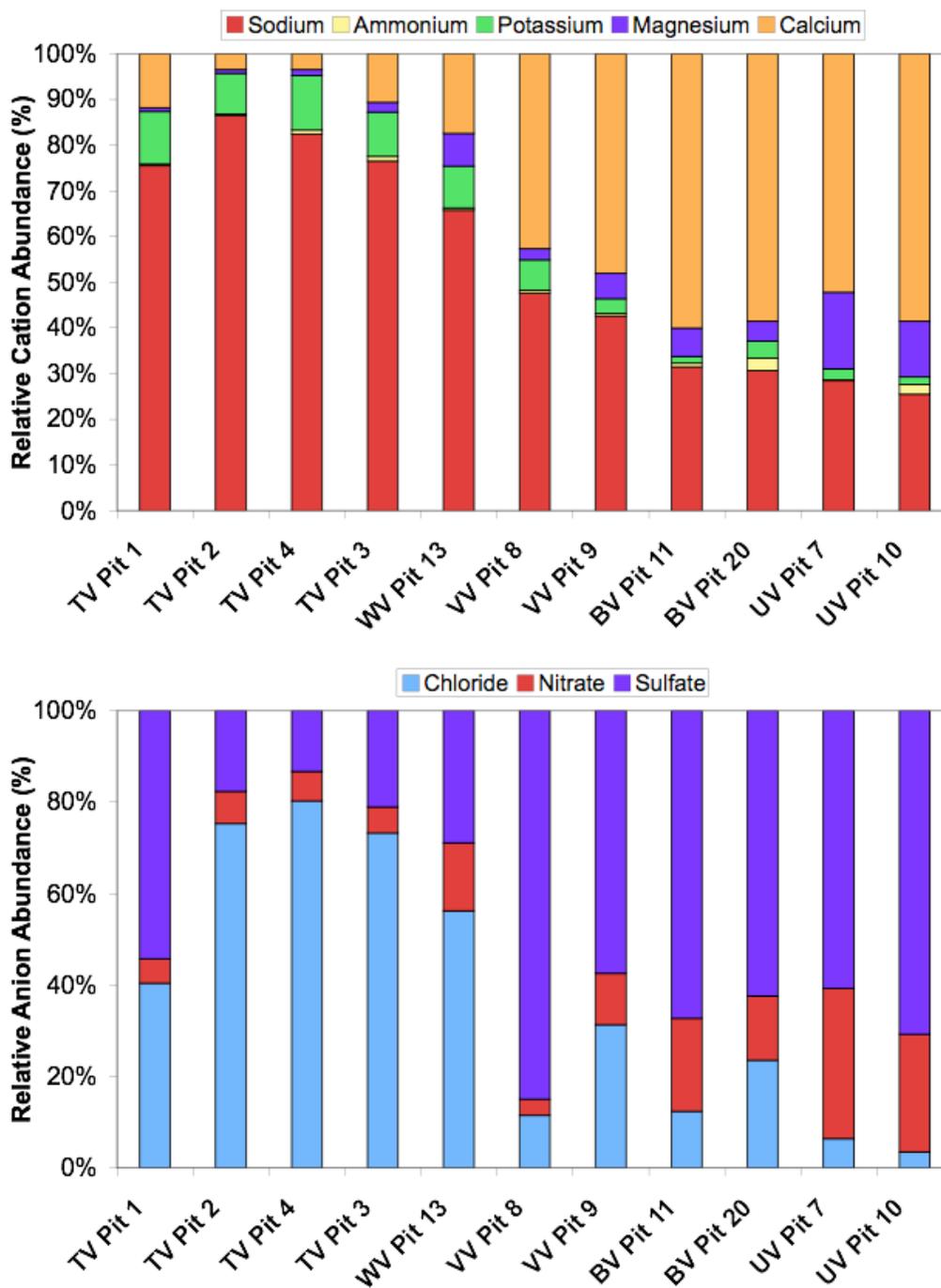


Figure 24: Relative abundance of anions (on top) and cations (on bottom) in the soils from each of the 11 pits analyzed from the McMurdo Dry Valleys

in the coastal thaw zone, after Na^+ and K^+ . Potassium concentration continued to decrease with elevation, from second in the coastal thaw zone to third or fourth in the inland mixed zone, to fourth of lowest concentration ion in the stable upper zone. Magnesium was steady between third and fourth most abundant for all three zones. Finally, ammonium was the least concentrated ion in the soils from the both the coastal thaw zone and inland mixed zone. In the upper stable zone, ammonium varied between the third, fourth and fifth most abundant cation. Barium, if present, was always the least abundant cation and not shown in Figure 24.

Elevation versus Concentration: Combining the concentration of a single ion in all soil horizons of a single pit and dividing by the number of horizons determined the average amount of each ion present in a pit. The average ion concentration per pit was then plotted versus the elevation of that pit. Magnesium, calcium, nitrate and sulfate all showed a good correlation ($R^2 = 0.6814, 0.8123, 0.8364, \text{ and } 0.8131$, respectively) with an increase in concentration with elevation (Figure 25). Thus increase was likely the result of the increase aridity with elevation which allowed these ions to accumulate more without being washed away. Likewise, phosphate, carbonate and bicarbonate show a good correlation ($R^2 = 0.4838, 0.5081, \text{ and } 0.4420$ respectively) but decrease in concentration with elevation. Phosphate is an indicator of biological activity, which is expected to decrease from the wetter coastal thaw zone where biological activity is higher to the more arid stable upland zone where biological activity becomes more scarce. There was no correlation ($R^2 = 0.2741$ or less) found between average ion concentration and elevation for sodium, ammonium, potassium, or chloride. The lack of any correlation for sodium and chloride may be due to competition of accumulation from the va-

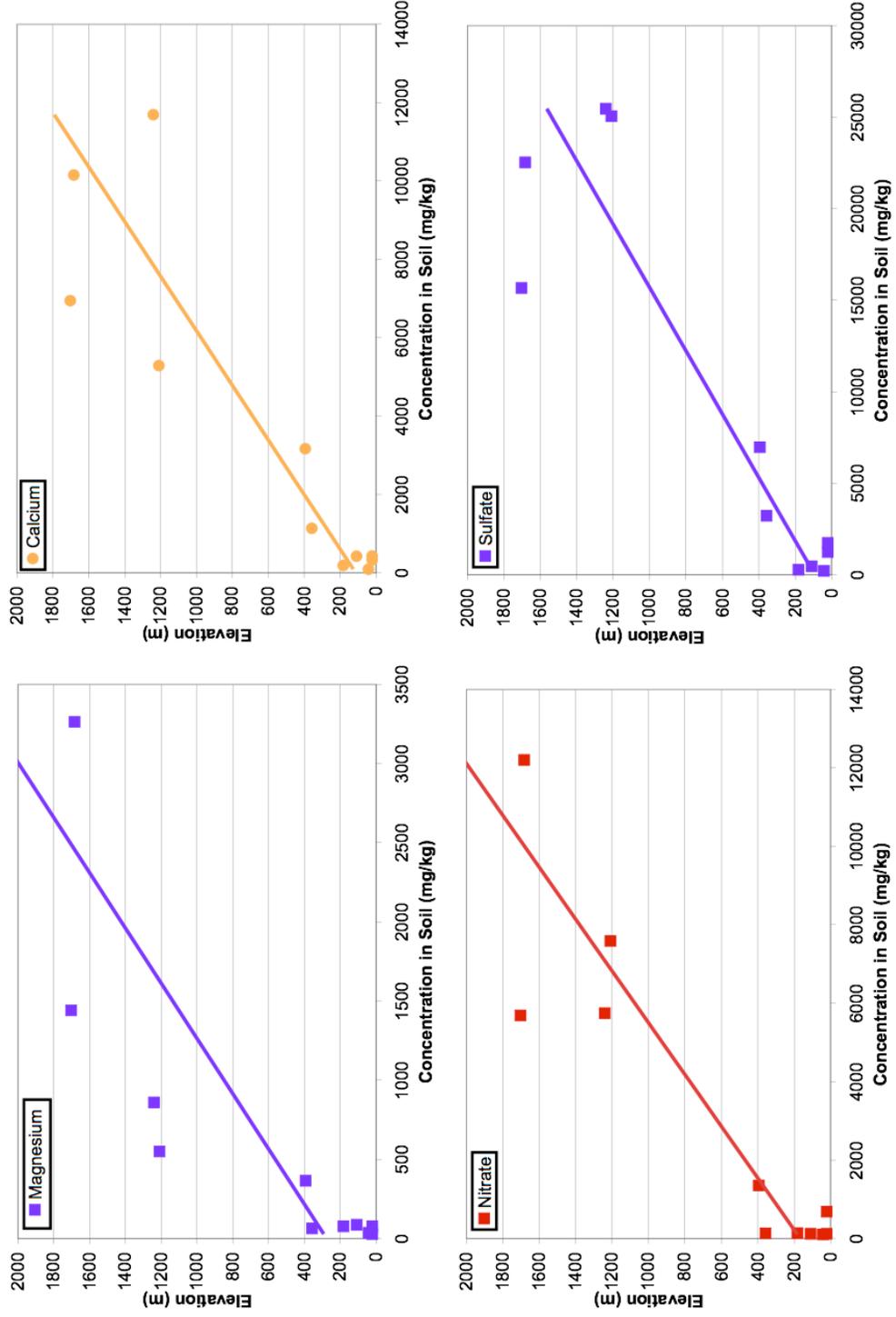


Figure 25: Pit elevation (in m) versus total concentration of ions in the soil (in mg/kg) of: magnesium (top left), calcium (top right), nitrate (bottom left) and sulfate (bottom right)

riety of sources for these ions (for example, marine aerosols in the coastal thaw zone as well as snowfall from the polar plateau in the inland mixed and stable upland zones). As for ammonium the lack of correlation may be due to the relative scarcity of this ion in the MDV.

Overall, when the average total ionic strength (calculated from Equation 8) for each pit was plotted versus elevation, there was a strong correlation ($R^2 = 0.9005$) indicating an increase in ionic strength with increased elevation. This indicates an overall increase in soluble salts with increased elevation. The increase in soluble salts with elevations was as expected from the increase in aridity from the coastal thaw zone to the inland mixed zone to the stable upland zone which allowed for less ion migration due to less moisture to wash away the soluble salts.

2.4.3 pH, Conductivity and Ionic Strength

In addition to analyzing the soils from the McMurdo Dry Valley to determine the soluble ion content, the soil solution pH, electrical conductivity were measured and the ionic strength was calculated. Analysis of these other soil properties is important to allow for a better overall understanding of the soil from this environment. The results from each analysis is discussed and a comparison is made between the properties in the McMurdo Dry Valley soils and the soil from the North Polar Region of Mars.

pH: The pH of all soil samples was measured with a commercial pH probe. The pH probe was calibrated each day prior to analysis. The slope for the pH calibration varied from 96.2 to 99.1 over the course of this analysis.

Figure 26 depicts the pH profiles for all 11 pits. Antarctica soils are often classified as alkaline [35], however, as seen in Figure 26, the pH varies widely,

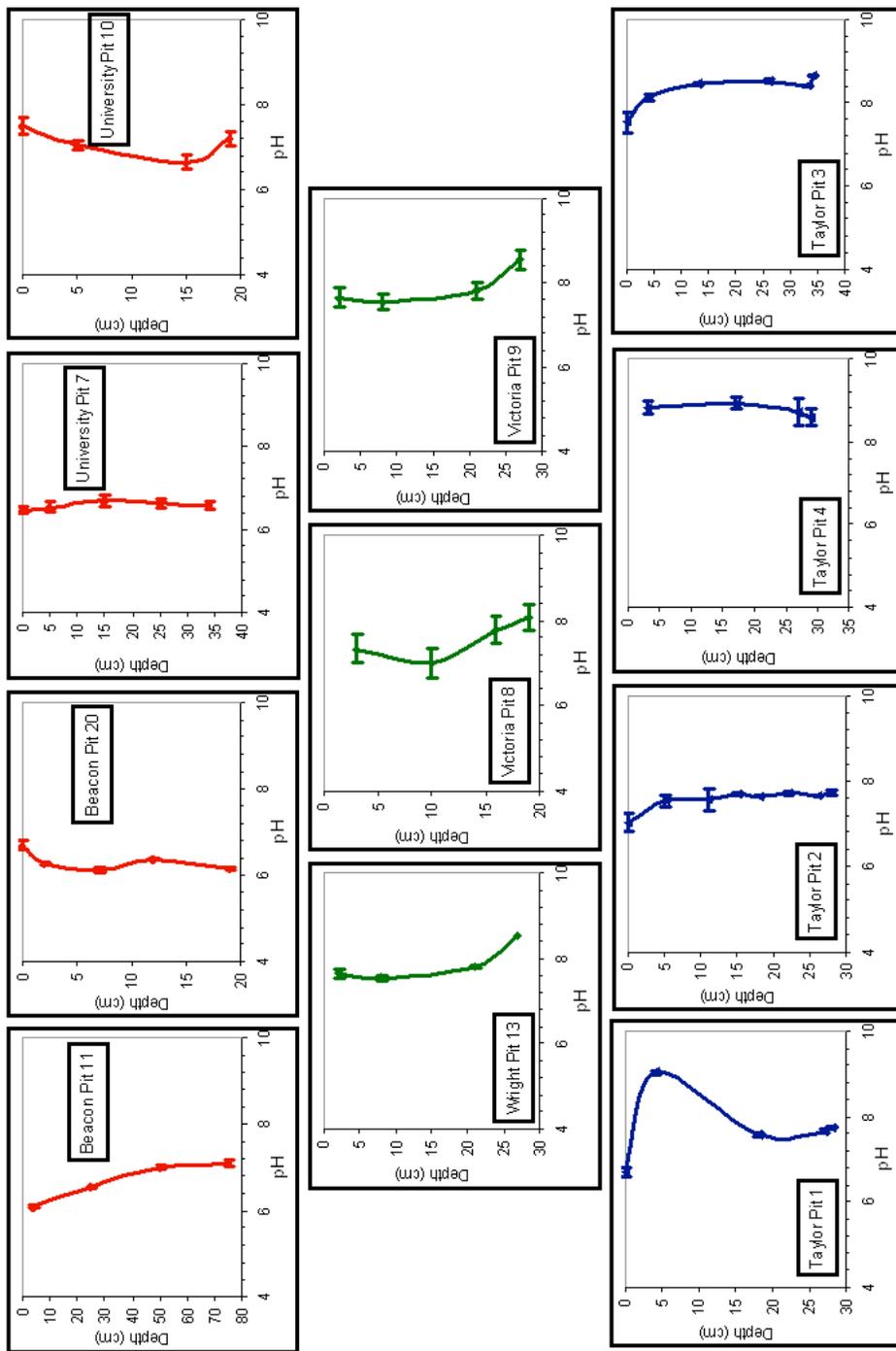


Figure 26: pH profiles of the MDV soil leachates from all 11 pits. One gram of each soil was leached in 25 mL of 18.2 mΩ water for ~24 hours then filtered before the pH was measured with a commercially available pH probe.

by three units on the pH scale, from a low of 6.10 in a soil from Pit 11 in Beacon Valley to 9.03 in a soil from Pit 1 in Taylor Valley. The soils from the coastal thaw zone and the inland mixed zone do have a slightly alkaline pH with average pit pH ranging from 7.58 ± 0.23 to 8.77 ± 0.15 in the coastal thaw zone and 7.54 ± 0.46 to 8.60 ± 0.25 in the inland mixed zone. Soils from the stable upland zone are slightly acidic with average pit pH ranging from 6.58 ± 0.09 to 7.09 ± 0.35 . This finding is in slight disagreement with Campbell and Claridge [35] which states that soils from the inland mixed and stable upland zones have pHs slightly acidic from 6 to 6.5 and soils from the coastal thaw zone have slightly higher pHs, just over 7, due to the stronger marine influence.

Campbell and Claridge observed there is a good correlation between pH and the $\text{Cl}^-/\text{SO}_4^{2-}$ ratio in the soil, with a lower pH corresponding to a lower $\text{Cl}^-/\text{SO}_4^{2-}$ ratio. [35]. Plotting the ratio of $\text{Cl}^-/\text{SO}_4^{2-}$ for each pit as a function of average pH for the pit gave an R^2 value of 0.3795. A very good positive correlation was seen for the inland mixed zone pits only ($R^2 = 0.9890$), while there was very little correlation for either the coastal thaw zone or stable upland zone ($R^2 = 0.0887$ and 0.0005 , respectively). Within individual pits, *i.e.*, plotting the $\text{Cl}^-/\text{SO}_4^{2-}$ for a each soil horizon as a function of the pH for that soil horizon, there was a good positive correlation seen in Pit 9 of Victoria Valley ($R^2 = 0.9587$), Pit 7 in University Valley ($R^2 = 0.5927$) and both Pits 11 and 20 in Beacon Valley ($R^2 = 0.8529$ and 0.8682 , respectively). There was a decent positive correlation seen in Pit 4 of Taylor Valley ($R^2 = 0.4587$) and Pit 8 in Victoria Valley ($R^2 = 0.3855$) with a decent negative correlation seen in Pit 13 in Wright Valley ($R^2 = 0.3649$). No correlation was seen in Pits 1, 2, and 3 in Taylor Valley or Pit 10 in University Valley. Thus the observation by Campbell and Claridge [35] of a correlation between the

ratio of $\text{Cl}^-/\text{SO}_4^{2-}$ and pH only sometimes holds for the soils analyzed in this study.

Campbell and Claridge also note the pH of Antarctic soils does not appear to be related to the presence of carbonate minerals. [35]. This holds true for the soils analyzed in this study. There is no real correlation between the concentration of carbonate or bicarbonate and soil pH when looking at individual soil horizons within a pit. However, carbonate was detected in the coastal thaw zone and inland mixed zone and those pits did average a slightly basic pH (8.09 ± 0.54 and 8.01 ± 0.54 , respectively), while the stable upland zone had no detectable carbonate and averaged a slightly acidic pH of 6.86 ± 0.31 . This suggests that the soil has little to no buffering capacity and the pH is influenced mainly by the compositions of the soluble salts present.

The pH of the leached MDV soils collected at the pavement level down to a depth of 5 cm, varies considerably across the 11 pits studied from a low of 6.10 ± 0.03 in Pits 9 and 11 to a high of 9.03 ± 0.06 in Pit 1. The pH of the Martian surface soil, from zero to five cm in depth was determined by the WCL aboard the Phoenix Mars Lander (see Chapter 1) to be 7.7 ± 0.3 . Thus the pH of the Martian soil falls nicely within the range of soil pH at equivalent depths in this Mars analog environment.

Conductivity: Solution electrical conductivity was determined for all soil leachate solutions using either a commercial Orion conductivity probe (for Pit 20) or an external conductivity probe connected to the WCL electronics (for all other Pits). Figure 27 shows the conductivity profile for each of the 11 pits. For all 11 pits, the shape of the conductivity profiles is highly correlated to the shape of the profile of the dominant ion in each pit. Additionally, it can be seen that the conductivity of the soil samples increase with increasing

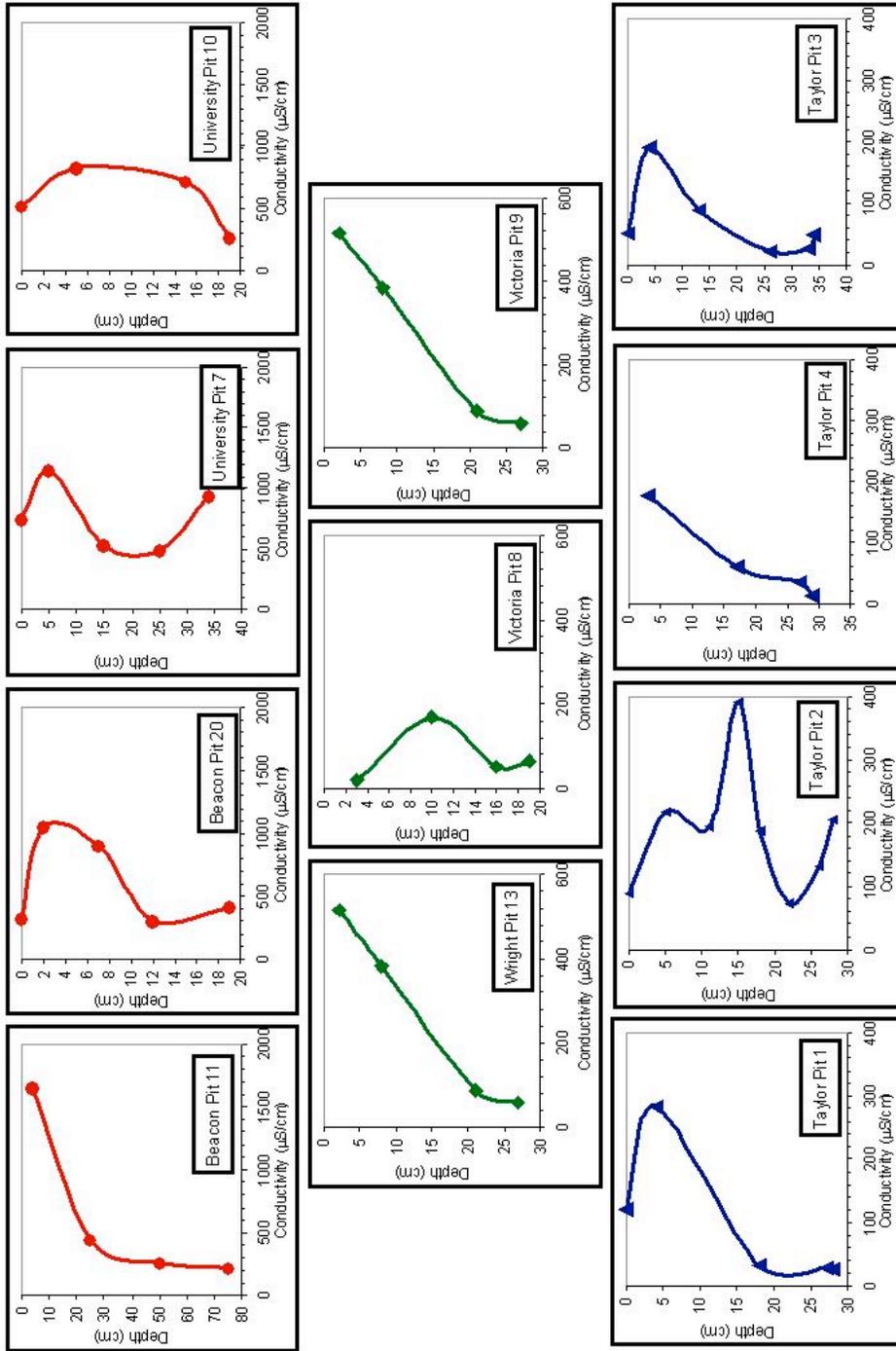


Figure 27: Electrical conductivity profiles of the MDV soil leachates from all 11 pits. One gram of each soil was leached in 25 mL of 18.2 mΩ water for ~24 hours then filtered before the conductivity was measured with a commercially available pH probe (Pits 1, 2, 3, 4, 7, 8, 9, 10, 11, and 13) or the conductivity probe in WCL (Pit 20).

elevation, with the lowest conductivity in soils from the coastal thaw zone and the highest from the soils from the stable upland zone. Higher conductivity indicates higher soluble salt concentration and this trend was as expected because of the increased aridity from coastal thaw zone to the stable upland zone which allows for greater salt accumulation as species are not as easily washed away.

Comparison of the average solution electrical conductivity of the Martian soil (at a depth of zero to five cm) determined by the WCL's conductivity sensor, $1635 \mu\text{S}/\text{cm} \pm 375 \mu\text{S}/\text{cm}$, to the solution electrical conductivity of the MDV soils at equivalent depth showed most MDV near pavement level soils possess a one to two order of magnitude lower conductivity than the Martian soil with only Pits 11 and 20 in Beacon Valley and Pit 7 in University Valley comparable (*i.e.*, on the same order of magnitude) conductivity to the Martian soil. Overall the soils from the coastal thaw zone and inland mixed zone had much lower conductivity than the Martian soil while soils from the stable upland zone, Pits 7, 10, 11 and 20, had higher overall conductivity and were closest to the conductivity of the soil on Mars.

The conductivity results were used to calculate the ionic strength of the solutions. The resulting ionic strengths calculated by this method could subsequently be compared to the ionic strengths determined from the IC and acid-base titration experiments. The results of the ionic strength calculations are discussed below.

Ionic Strength: The ionic strengths of the soil leachates were calculated two ways: from the IC and acid-base titration data (using Equation 7) and from the measured conductivity (using Equation 8). Figure 28 shows a comparison of ionic strengths as a function of depth calculated by both methods for Pit 2

in Taylor Valley (on top) and Pit 7 in University Valley (on bottom).

As seen in Figure 28, the profiles for ionic strength are as expected for Pit 2 in Taylor Valley with the ionic strength calculated from conductivity (μ_{exp}), which is known to encompass all charged species present, being greater for all soil horizons than the conductivity calculated from the IC (μ_m) where it was known that some species contributing to the ionic strength could not be quantified. It was possible to say with certainty that not all species were quantified because there was a difference between the total cation charge and total anion charge resulting in an anion deficiency in all pits (except Pit 11 where there was a cation deficiency). One species found to be present in soils from the MDV is iodate (IO_3^-) [36, 37] which was not analyzed for in the IC analysis of these soils. Thus iodate could account for some or all of the anion deficiency seen here.

However, the profile for ionic strength for Pit 7 (in University Valley) was not entirely as expected with three of the five soil horizons showing $\mu_{exp} > \mu_m$. Additionally, when looking at the profiles from all 11 pits, only the four pits from the coastal thaw zone had profiles for ionic strength as expected, with $\mu_m > \mu_{exp}$. Likewise, all pits from the inland mixed zone and the stable upland zone showed $\mu_{exp} > \mu_m$.

In-depth Look at Ionic Strength: A study was performed to determine a new constant for the Griffin-Jurinak relationship suitable for MDV soils from the inland mixed and stable upland zones where the soils have a high ionic strength and are dominated more by divalent than monovalent salts. Calibration curves were created from standards containing a single ion pair, Na^+ and Cl^- , and standards containing multiple ions (see Table 21). The correlation equation was $\mu = 0.0079\text{EC}$ ($R^2 = 99.83$) for the standards of NaCl only

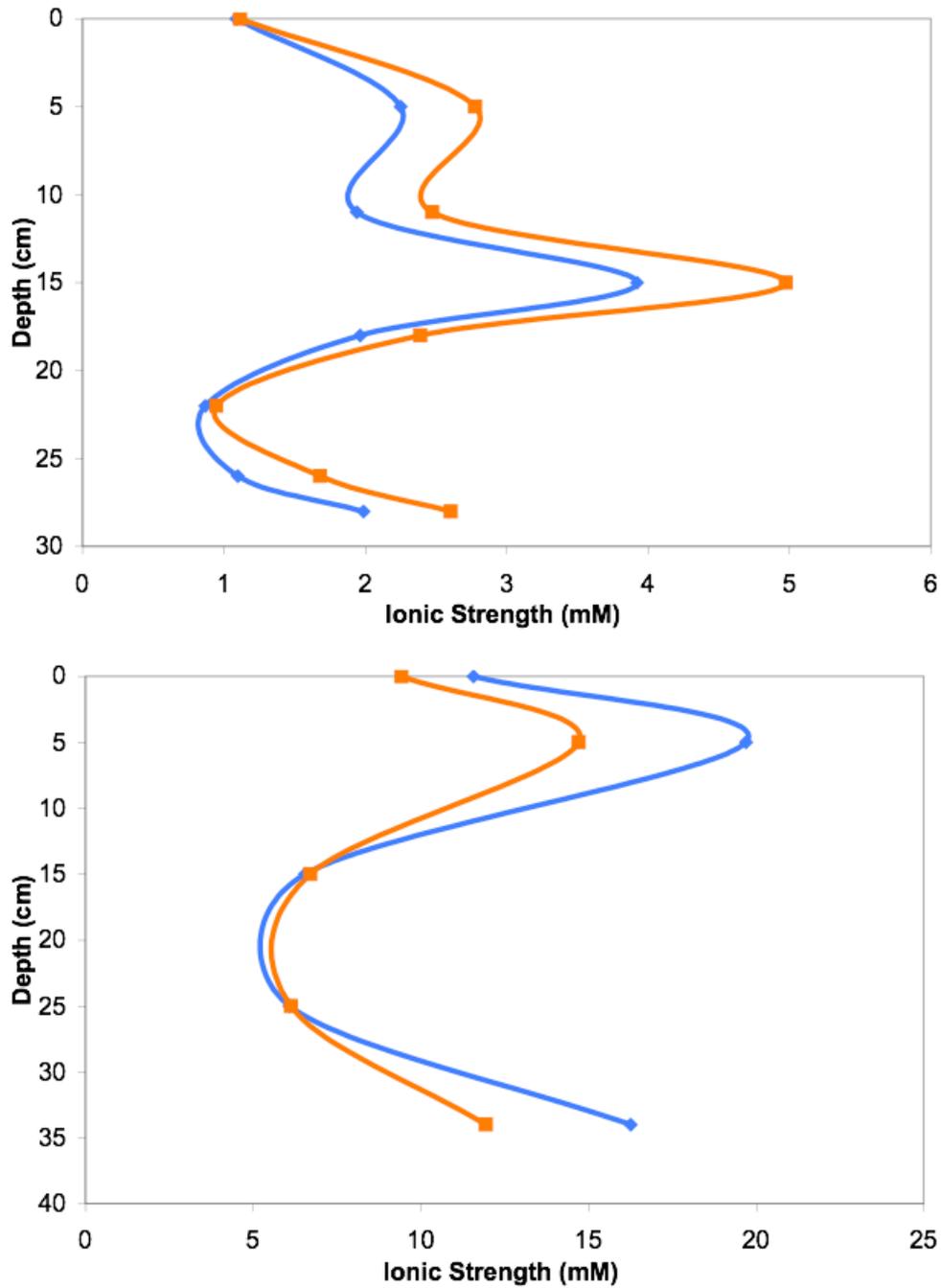


Figure 28: Ionic strength profiles of the MDV soil leachates (in mM) from Pit 2 in Taylor Valley (on top) and Pit 7 in University Valley (on bottom) as a function of depth (in cm) calculated by two separate methods: μ_{exp} (blue diamonds) and μ_m (orange squares)

and $\mu = 0.0149EC$ ($R^2 = 99.63$) for the standards containing multiple ions. These results indicate that two solutions with the same ionic strength can result in different electrical conductivities and therefore, it was shown that the concentration and types of ions present in solution affect the Griffin-Jurinak Relationship as discussed by Simón and Gracia. [47]

Using the new relationship, $\mu = 0.0149EC$, calculated from the multi-ion standards, the ionic strength of all ultraxerous soils was recalculated and the ionic strengths were approximately 15% greater than when calculated using the Griffin-Jurinak Relationship (Equation 8). This made the μ_m closer to μ_{exp} . However, $\mu_{exp} > \mu_m$ for the inland mixed zone and stable upland zone soils.

Overall, this study clearly indicates that the Griffin-Jurinak Relationship does not hold for soils in an extreme environment, such as the inland mixed and stable upland zones of the MDV, where the overall ion concentration is large and the soils are not dominated by monovalent ions. Initial attempts to correct this relationship using a multi-ion standard brought the ionic strength values calculated by the two methods closer but was not successful in determining the correct relationship for these soils. Further experimentation must be performed to determine a variation of the Griffin-Jurinak Relationship which can be used for extreme environment soils, such as the upper valleys of Antarctica.

2.4.4 Comparison of MDV Soils to Martian Soil

Soil samples from the three microclimate zones in the McMurdo Dry Valleys (MDV) were analyzed for soluble ion content, soil pH, solution electrical conductivity and ionic strength. The results from this analysis were then compared to the results from the WCL analysis of the Martian soil (see Chapter 2) to compare these two extreme environments. Table 23 compares the geo-

chemical properties of the of the Martian soil from the Phoenix Lander site determined by WCL to that of the soils from the coastal thaw zone (CTZ) and the stable upland zone (SUZ) of the MDV determined by ion chromatography. The soils from the inland mixed zone (IMZ) of the MDV were excluded from this comparison due to the limited number of soil samples collected and analyzed. [51]

The soil properties from the MDV were compared to the Mars data in two ways. First, the soil samples from only the top 5 cm of the pits in the CTZ and SUZ were compared to the Mars data. This comparison represents the soils in the MDV at the analogous depth to the soils analyzed on Mars. However, the soils from Mars were analyzed to a depth of only 5 cm because the ice-table was reached at this depth. Thus the two soil samples represent an average of the soil chemical properties from the pavement to the ice-table. Thus soil samples from all depths from the pavement to the permafrost in the pits from the CTZ and SUZ were averaged. This comparison represents the average chemical properties in the soils from pavement to permafrost from the CTZ and SUZ of the MDV. [51] Both methods of comparison are discussed below.

Comparison to the top 5 cm of soil: The pH of the Martian soil at the Phoenix Lander site most closely matched the pH of the soils from the coastal thaw zone. The soils from the stable upland zone were slightly more acidic than the Martian soil. The electrical conductivity of the Martian soil was an order of magnitude larger than the conductivity of the CTZ soils indicating the soils were less salty in the CTZ than on Mars. The conductivity of the SUZ soil and the Martian soil were very similar, indicating these soils had similar ionic strengths. [51]

Table 23: Comparison of soils from the north polar region of Mars to soils from the CTZ and the SUZ of the MDV

| Geochemical Property | Mars ^a TOp 5 cm Soils (n = 2) | MDV CTZ ^b Top 5 cm Soils (n = 7) | MDV SUZ ^b Top 5 cm Soils (n = 7) | MDV CTZ ^b All Soils (n = 23) | MDV SUZ ^b All Soils (n = 18) |
|--|--|---|---|---|---|
| pH | 7.7 ± 0.3 | 7.8 ± 0.9 | 6.7 ± 0.4 | 8.1 ± 0.5 | 6.7 ± 0.4 |
| Conductivity (μS/cm) | 1635 ± 375 | 283 ± 97 | 1319 ± 525 | 107 ± 54 | 650 ± 84 |
| Na ⁺ (mM) | 1.4 ± 0.3 | 2.6 ± 0.5 | 3.3 ± 1.1 | 1.2 ± 0.1 | 1.6 ± 0.2 |
| NH ₄ ⁺ (mM) | N.D. ^c | 0.023 ± 0.006 | 0.195 ± 0.192 | 0.0103 ± 0.0023 | 0.1067 ± 0.0210 |
| K ⁺ (mM) | 0.39 ± 0.08 | 0.21 ± 0.09 | 0.16 ± 0.11 | 0.087 ± 0.003 | 0.08 ± 0.03 |
| Mg ²⁺ (mM) | 3.3 ± 1.7 | 0.06 ± 0.02 | 1.41 ± 0.56 | 0.016 ± 0.002 | 0.56 ± 0.05 |
| Ca ²⁺ (mM) | 0.6 ± 0.3 | 0.23 ± 0.13 | 4.98 ± 0.68 | 0.056 ± 0.003 | 1.91 ± 0.20 |
| Cl ⁻ (mM) | 0.47 ± 0.09 | 1.06 ± 0.22 | 2.28 ± 1.42 | 0.48 ± 0.02 | 1.91 ± 0.20 |
| NO ₃ ⁻ (mM) | N.D. ^c | 0.06 ± 0.01 | 2.30 ± 1.3 | 0.025 ± 0.002 | 1.14 ± 0.08 |
| SO ₄ ²⁻ (mM) | 5.4 ± 0.78 | 0.27 ± 0.19 | 5.62 ± 1.93 | 0.06 ± 0.01 | 2.1 ± 0.1 |
| [Na ⁺]:[K ⁺] | 2:1 to 6:1 | 7:1 to 26:1 | 8:1 to 88:1 | 12:1 to 16:1 | 13:1 to 36:1 |
| [Na ⁺]:[Mg ²⁺] | 1:1 to 6:1 | 6:1 to 31:1 | 0.4:1 to 1:1 | 19:1 to 25:1 | 0.7:1 to 1:1 |
| [Na ⁺]:[Ca ²⁺] | 1:1 to 5:1 | 0.01:1 to 0.04:1 | 0.2:1 to 0.9:1 | 0.01:1 to 0.02:1 | 0.3:1 to 0.4:1 |
| [Mg ²⁺]:[K ⁺] | 3:1 to 16:1 | 0.1:1 to 0.7:1 | 3:1 to 39:1 | 0.2:1 to 0.2:1 | 5:1 to 12:1 |
| [Mg ²⁺]:[Ca ²⁺] | 2:1 to 17:1 | 0.1:1 to 0.8:1 | 0.2:1 to 0.5:1 | 0.2:1 to 0.3:1 | 0.2:1 to 0.4:1 |
| [Mg ²⁺]:[Cl ⁻] | 0.5:1 to 2:1 | 0.03:1 to 0.1:1 | 0.2:1 to 2:1 | 0.03:1 to 0.04:1 | 0.2:1 to 0.4:1 |
| [Ca ²⁺]:[K ⁺] | 0.6:1 to 3:1 | 0.3:1 to 3:1 | 16:1 to 113:1 | 0.6:1 to 0.7:1 | 16:1 to 42:1 |
| [Cl ⁻]:[Na ⁺] | 1:1 to 3:1 | 0.3:1 to 0.6:1 | 0.2:1 to 2:1 | 0.4:1 to 0.5:1 | 1:1 to 2:1 |
| [Cl ⁻]:[K ⁺] | 5:1 to 11:1 | 3:1 to 11:1 | 3:1 to 74:1 | 5:1 to 6:1 | 16:1 to 42:1 |
| [Cl ⁻]:[Ca ²⁺] | 3:1 to 12:1 | 2:1 to 13:1 | 0.2:1 to 0.9:1 | 8:1 to 9:1 | 0.8:1 to 1:1 |
| [SO ₄ ²⁻]:[Na ⁺] | 3:1 to 6:1 | 0.03:1 to 0.2:1 | 0.8:1 to 3:1 | 0.04:1 to 0.8:1 | 1:1 to 2:1 |
| [SO ₄ ²⁻]:[K ⁺] | 10:1 to 20:1 | 0.3:1 to 4:1 | 14:1 to 51:1 | 0.6:1 to 0.8:1 | 19:1 to 42:1 |
| [SO ₄ ²⁻]:[Mg ²⁺] | 1:1 to 4:1 | 1:1 to 12:1 | 2:1 to 9:1 | 3:1 to 5:1 | 3:1 to 4:1 |
| [SO ₄ ²⁻]:[Ca ²⁺] | 5:1 to 21:1 | 0.2:1 to 5:1 | 0.7:1 to 2:1 | 0.8:1 to 1:1 | 1:1 to 1:1 |
| [SO ₄ ²⁻]:[Cl ⁻] | 1:1 to 3:1 | 0.1:1 to 0.6:1 | 1:1 to 9:1 | 0.1:1 to 0.2:1 | 1:1 to 1:1 |

^a WCL ISE response when 1 cm³ of soil with assumed density of 1 g/cm³ was added to 25 mL of pure water

^b IC result of soil leachate when 1 g of soil was leached in 25 mL of pure water for ~24 hours

^c N.D. = Not Detected. The value were below the instrument's limit of detection for that ion

When comparing the individual soluble ions in the soils from Mars and the soils from the CTZ, Na^+ , K^+ , and Ca^{2+} were on the same order of magnitude in concentration. The concentration of Cl^- was barely an order of magnitude higher in the CTZ, while the concentrations of SO_4^{2-} and Mg^{2+} were one and two orders of magnitude lower in the CTZ, respectively. [51] Since the concentrations of NH_4^+ and NO_3^- were not determined on Mars it was not possible to make direct comparisons to these ions. However, in the case of NO_3^- it was estimated that $[\text{NO}_3^-] \leq 1 \text{ mM}$ on Mars based on the measured conductivity. [52] Using this estimate it was determined that the soil from the CTZ may be on the same order of magnitude in concentration. [51]

When comparing the individual soluble ions in the soils from Mars and the soils from the SUZ, Na^+ , K^+ , Mg^{2+} and SO_4^{2-} were on the same order of magnitude in concentration. The other ions NH_4^+ , Ca^{2+} , Cl^- and NO_3^- were higher in concentration in the SUZ as compared to Mars. There was an order of magnitude more Ca^{2+} and Cl^- , and at least an order in magnitude more NO_3^- assuming $\leq 1 \text{ mM}$. No direct comparison could be made to NH_4^+ which was not detected on Mars by WCL. [51]

In addition to comparing the concentrations of ions in the soils from these extreme environments, the ratios of these ions were also compared. The range of ratios were calculated from the ion concentrations and corresponding standard deviations. (The ratios for chloride were determined using the combined concentrations of Cl^- and ClO_4^- , though perchlorate was not discussed in this chapter and therefore excluded from the table of comparisons, Table 23.) There were six similar ratios between Mars and the CTZ: $\text{Na}^+/\text{Mg}^{2+}$, $\text{Ca}^{2+}/\text{K}^+$, Cl^-/K^+ , $\text{Cl}^-/\text{Ca}^{2+}$, $\text{SO}_4^{2-}/\text{Mg}^{2+}$ and $\text{SO}_4^{2-}/\text{Ca}^{2+}$. All of the other ratios were lower in the CTZ than on Mars except Na^+/K^+ , which was higher. Likewise, there were nine similar ratios between Mars and the

SUZ: $\text{Na}^+/\text{Mg}^{2+}$, $\text{Mg}^{2+}/\text{K}^+$, $\text{Mg}^{2+}/\text{Cl}^-$, $\text{Ca}^{2+}/\text{Na}^+$, Cl^-/K^+ , $\text{SO}_4^{2-}/\text{Na}^+$, $\text{SO}_4^{2-}/\text{K}^+$, $\text{SO}_4^{2-}/\text{Mg}^{2+}$, and $\text{SO}_4^{2-}/\text{Cl}^-$. The Na^+/K^+ ratio was again higher in the SUZ as was the $\text{Ca}^{2+}/\text{K}^+$ ratio while the others were lower. These similar ion ratios indicated similar accumulation and depletion pathways for the species in both environments. [51]

Comparing the chemical properties of the top 5 cm soils from both the CTZ and the SUZ of the MDV to Mars, both had the same number of ions in the same order of magnitude concentration range. The CTZ had a similar soil pH, while the SUZ had a similar conductivity and a higher number of overlapping ion ratios. This would indicate that the SUZ soils from the top 5 cm were a closer match to the soils on Mars than the CTZ soils from the top 5 cm. [51]

Comparison to the Average of All Soils: Comparison of the pH of the Martian soil at the Phoenix Lander site most closely matched the pH of the soils from the coastal thaw zone averaged over the entire pit. The soils from the stable upland zone were slightly more acidic than the Martian soil. The electrical conductivity of the Martian soil was an order of magnitude larger than the conductivity of the SUZ soils and two orders of magnitude larger than the conductivity of the CTZ soils, thus indicating the soils in the MDV were less salty than the soil on Mars. [51]

When comparing the individual soluble ions in the soils from Mars and the soils from averaging all soil horizons in the CTZ, some of the trends were similar to looking at just the top 5 cm from the CTZ. For example, Na^+ was on the same order of magnitude in concentration in both locations. However, Cl^- was also on the same order of magnitude in concentration. Again the concentrations of NH_4^+ and NO_3^- were not determined on Mars and it was

not possible to make direct comparisons to these ions, but using the estimated $[\text{NO}_3^-]$ of ≤ 1 mM on Mars it was determined that the soil from the CTZ may be on the same order of magnitude in concentration. Differences between comparing only the top 5 cm and the average of all the soils included differences in the concentrations of the ions K^+ and Ca^{2+} which were an order of magnitudes lower and Mg^{2+} was two orders of magnitude lower in the CTZ compared to Mars. [51]

Again, when comparing the individual soluble ions in the soils from Mars and the soils from averaging all soils in the SUZ, some of the trends were similar to looking at just the top 5 cm for the SUZ. Once again the concentrations of Na^+ and SO_4^{2-} were on the same order of magnitude in both locations and the concentrations of Ca^{2+} , Cl^- , and NO_3^- all higher in concentration by at least an order of magnitude (assuming $[\text{NO}_3^-] \leq 1$ mM on Mars). Additionally, comparison could not be made for the ion NH_4^+ . However, the concentrations of K^+ and Mg^{2+} which were on the same order of magnitude for Mars and the SUZ when looking at only the top 5 cm of soil in the SUZ were lower in concentration each by an order of magnitude when comparing the average of all soils from the SUZ. [51]

In addition to comparing the concentrations of ions in the soils from these extreme environments, the ratios of these ions were also compared. There were four similar ratios between Mars and the CTZ: $\text{Ca}^{2+}/\text{K}^+$, Cl^-/K^+ , $\text{Cl}^-/\text{Ca}^{2+}$ and $\text{SO}_4^{2-}/\text{Mg}^{2+}$. All of the other ratios were lower in the CTZ than on Mars except Na^+/K^+ and $\text{Na}^+/\text{Mg}^{2+}$, which was higher. This was similar to what was seen when comparing only the top 5 cm from this zone. Likewise, there were six similar ratios between Mars and the SUZ: $\text{Na}^+/\text{Mg}^{2+}$, $\text{Mg}^{2+}/\text{K}^+$, Cl^-/Na^+ , $\text{SO}_4^{2-}/\text{K}^+$, $\text{SO}_4^{2-}/\text{Mg}^{2+}$ and $\text{SO}_4^{2-}/\text{Cl}^-$. The Na^+/K^+ ratio was again higher in the SUZ as well as $\text{Ca}^{2+}/\text{K}^+$ and Cl^-/K^+ while the others

were lower. Again this was similar to what was seen for the top 5 cm of this zone. [51]

Comparing the chemical properties of all the soils from both the CTZ and the SUZ of the MDV to Mars, both had the same number of ions in the same order of magnitude concentration range, same as seen for the top 5 cm soils. As with the top 5 cm soils, the CTZ again had a similar soil pH. When averaging all the soils in these zones the conductivities are both an order of magnitude lower than Mars, but the conductivity of the SUZ soils was closer to the conductivity of the Martian soil than the CTZ conductivity. The SUZ also a higher number of overlapping ion ratios, same as with the top 5 cm soils. This indicated the average for all the soils in the SUZ was a closer match to the soils on Mars. Regardless of how the soils from the MDV were compared to the soils on Mars, looking at the average of the soils from only the top 5 cm or looking at the average of all soils from the pavement to the permafrost the result was the same. The soils from the stable upland zone have chemical properties closer the soils from Mars at the Phoenix Lander site. [51]

2.5 Conclusions

The McMurdo Dry Valleys (MDV) of Antarctica are considered by some to be the most Mars-like place on Earth due to among other things its low temperatures and high aridity. [30, 31, 32, 33, 34] As part of the 2007 International Polar Year, pits were dug and soil samples were collected from the various soil horizons from the pavement level down to the permafrost layer (or in the case of Pit 20 into the permafrost layer) from 11 different locations scattered throughout the MDV three microclimate zones: coastal thaw zone (CTZ), inland mixed zone (IMZ) and stable upland zone (SUZ). These soils were intended to fulfill the cataloging portion of the preflight C, C, and C process for

Phoenix's Wet Chemistry Laboratory (WCL) as well as provide additionally insight into this unique soil environment on Earth.

The soils collected were analyzed by a variety of analytical techniques. The WCL analysis was originally designed to mimic the analysis performed on Mars and provide a catalog of analog soils. However, it was discovered that some of the ISEs in the WCL testbed used for this analysis, including the Li^+ reference, had become less selective overtime due to aging and extended usage. This caused the WCL to give less than reliable results. Therefore, it was decided it would be unwise to create a catalog of the soils using this data.

In addition to the ISEs in WCL, ion chromatography (IC) and acid-base titration were also used to determine the soluble ionic species present in the MDV soils. The results from this analysis were considered much more reliable than the WCL data and was used for all comparisons, pit-to-pit, zone-to-zone and MDV to Mars. In addition, the pH and conductivity of the soil leachate solutions were also measured and the ionic strength of these solutions were calculated. These chemical properties of the soils were also compared to the Martian soil.

In comparing the soils from the three microclimate zones of the MDV the same nine ions, Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , HCO_3^- , and SO_4^{2-} were present in measurable quantities in all 11 pits. Other ions present in some locations included: Ba^{2+} , CO_3^{2-} and PO_4^{3-} . The dominant ions in the coastal thaw zone were Na^+ and Cl^- in the form of halite brought into this zone by marine aerosols, while the dominant ions in the stable upland zone were in Ca^{2+} and SO_4^{2-} in the form of gypsum (as confirmed by XRD). These finding compared well with the findings for other soils analyzed in these microclimate zones.

All of the soil sampled in the three micro-climate zone had a moderate pH

ranging from 6.10 to 9.12, with soils in the pits from the CTZ and IMZ being slightly more basic, averaging $\text{pH } 7.58 \pm 0.23$ to 8.77 ± 0.15 per pit, and soils from the pits in the SUZ being slightly more acidic, averaging $\text{pH } 6.58 \pm 0.09$ to 7.09 ± 0.35 per pit. The majority of the pits, Pits 1, 3, 4, 9, 11, 13, and 20 showed a similar soil profile with the highest conductivity and therefore the highest ionic strength, present just below the pavement level and then decreasing with depth down to the permafrost layer. The ionic strength also showed a positive correlation with elevation, with the salt content increasing from the pits at low elevations in the CTZ up to the pits at high elevation in the SUZ. This was as expected from the increase aridity with elevation which would cause there to be less ion migration and therefore increase ion accumulation.

One interesting discovery when calculating the ionic strength of these extreme environment soils was the difference between the μ_{exp} and the μ_m . For the soils in the CTZ, the $\mu_m > \mu_{exp}$, indicating that not all soluble ionic species had been identified/quantified from the experimental methods. However, for soils from both the IMZ and SUZ the $\mu_m < \mu_{exp}$, indicating that the Griffin-Jurinak relationship (Equation 8) did not hold for soils and a variation of this relationship with a new constant is necessary for soils from this extreme environment.

Comparison of the Martian soil from the Phoenix Lander site to the soils from the CTZ and SUZ was performed in two ways. First, only the soils from the top 5 cm of the pits were averaged for each zone. Next, all of the soils from the pavement to the permafrost were averaged for each zone. Both methods of comparison yielded similar results. The soils from the CTZ were close in pH to Mars, while the SUZ soils were slightly more acidic. The conductivity of the soils from the top 5 cm in the SUZ were similar to the Martian soil, while

the soils from the CTZ were an order of magnitude lower, indicating the salt content on Mars was greater than the CTZ but similar to the SUZ. [51]

The concentration of the individual ions, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , and SO_4^{2-} , could be directly compared between the soils from the MDV climate zones and those from Mars. There was not more than two orders of magnitude difference in concentrations between the individual ions in both zones in the MDV and the concentrations on Mars at the Phoenix Lander site. There was no NH_4^+ found at measurable quantities in the soils on Mars, however, this ion was present in both the CTZ and SUZ of the MDV. Likewise, the $[\text{NO}_3^-]$ could not be determined on Mars, but was estimated to be ≤ 1 mM which would be less than the concentration seen in the SUZ. When making comparisons between these two extreme environments, it must be remembered these locations are on two separate planets and concentrations varying by one to two orders of magnitude between these two environments are not that different. In addition to comparing the total concentration of individual ions, the ratios of these ionic species were also compared and more ratios were similar for the SUZ than the CTZ. Considering all these chemical properties collectively, it was shown that the soils from the SUZ were more similar to the Martian soil at the Phoenix Lander site. [51]

The soil analyzed on Mars was sampled from a small location in the north polar region. Currently there is little evidence to support a hypothesis that the soil on Mars is homogeneous. While this study suggests the soil from the stable upland zone is most similar to the soil at the Phoenix Lander site, it may not be the most similar to the soil in other locations on Mars. However, based on what is known of the Martian soil to date, the soil from the stable upland zone may be called a suitable soil analog.

3 Perchlorate in the McMurdo Dry Valleys

3.1 Introduction

In 2008, the Phoenix Mars Scout Lander discovered the presence of 0.6 wt. % perchlorate on the surface and near subsurface of Mars near the Martian north pole. It has been proposed the perchlorate is in the form of $\text{Mg}(\text{ClO}_4)_2$ or $\text{Ca}(\text{ClO}_4)_2$ based upon the distribution of cations also found in the soil. [19] However, this has yet to be verified. The discovery of perchlorate on Mars led to the analysis of the McMurdo Dry Valley (MDV) soils, collected by a team of Phoenix scientists as part of the International Polar Year (IPY), for perchlorate. Its presence would strengthen the validity of MDV soil as a suitable Martian analog.

This chapter provides a background of perchlorate and its potential health risks along with the previously known locations of natural sources of perchlorate on Earth and a discussion of its possible pathway of formation. This is followed by the experimental parameters for the analysis of the MDV soil for perchlorate by ion chromatography. The chapter concludes with a discussion of the results of this analysis and the possible implications of discovering perchlorate in the MDV.

3.2 Background

In the past several years, perchlorate has received considerable attention. It has been shown that the presence of perchlorate in drinking water and its subsequent uptake from groundwater into foodstuffs is harmful to the human body. It was believed for many years that perchlorate contamination was due mainly to anthropogenic sources, for example rocket fuel and fireworks, as well as a singular natural source, in the caliche nitrate deposits of the Ata-

cama Desert which were mined for their use as fertilizer in several countries including the United States. Subsequently, it has been found that natural perchlorate exists outside the Atacama, in locations such as Death Valley in California as well as outside the Earth, with 0.6% presence on the surface of Mars. Despite the growing number of locations where natural perchlorate has been located, the mechanistic pathway leading to its formation has still yet to be fully understood. The following sections discuss the health risks of perchlorate and the locations on Earth and Mars where natural perchlorate has previously been discovered. This is followed by a discussion of the hypothesized mechanistic pathway of formation of this compound and isotopic analysis studies used to constrain the possibilities.

3.2.1 Health Risks

Perchlorate is recognized by the Environmental Protection Agency (EPA) as an emerging contaminant. An emerging contaminant is defined as “a chemical or substance that is characterized by a perceived, potential or real threat to human health or the environment or a lack of public health standards.” [53] Perchlorate is highly soluble and relatively stable in water. Therefore, perchlorate can easily penetrate into ground water and contaminate drinking water sources and food supplies. The main health risk of perchlorate is its ability to inhibit the thyroid gland from absorbing iodine into the bloodstream and transporting it throughout the human body. This effect is temporary and reversible, meaning that once exposure of perchlorate to the body is eliminated the thyroid gland’s ability to absorb and transport iodine is restored. However, there is still concern about exposure to young children, people with poor iodine nutrition, and especially pregnant women as it can affect the unborn child. [54]

3.2.2 Locations of Natural Perchlorate on Earth

Perchlorate comes from two main sources, natural and anthropogenic. Since perchlorate salts (HClO_4 , NH_4ClO_4 , NaClO_4 , and KClO_4) are common oxidizers, the main sources of anthropogenic perchlorate are found as solid propellants, munitions, fireworks, matches and road signal flares. Other anthropogenic sources include airbag initiators, disinfectants and herbicides. [53] Over the past few years there has been much discussion surrounding the occurrence of natural perchlorate and its formation process. Natural perchlorate was first discovered in the caliche ore deposits of the Atacama Desert in Chile. [25, 55] Other natural sources of perchlorate have also been verified throughout North and South America in natural mineral deposits [56, 57] and groundwater [58, 59, 60, 61, 62, 63]. In most sites it is not possible to preclude the possibility of contamination from anthropogenic sources. However, the Atacama perchlorate as well as perchlorate recently found in arctic snow in Devon Island, Canada, [64] are known to be natural sources due to their remote locations completely isolated from exposure to manufactured perchlorate. Both of these locations can be classified as extreme environments. Therefore, the McMurdo Dry Valleys are a likely location for the presence of natural perchlorate.

3.2.3 Perchlorate Formation Pathway and Isotopic Analysis

Analysis of the isotopic oxygen and/or chloride signature on samples of perchlorate can be used to determine whether the perchlorate comes from an anthropogenic or natural source. In addition to the determination as to the origin of the perchlorate, it has been shown that the isotopic analysis can also provide insight into the pathway of formation of natural perchlorate. A discussion of the isotopic analyses performed on samples of man-made and natural perchlorate is discussed below.

Suggested Perchlorate Formation Pathways: For many years prior to isotopic studies, it was suggested perchlorate forms atmospherically by one of the following three mechanistic pathways. Back in 1975, Simonailis and Heicklen suggested that perchloric acid forms in the stratosphere in a three-body reaction of chloride, oxygen gas and ozone forming chlorate and oxygen gas (Equation 9).

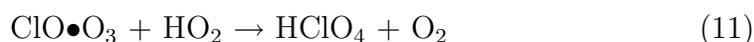


This was followed by the reaction of chlorate with hydroxide radical forming perchloric acid (Equation 10).



At that time, there was no evidence for or against the presence of perchloric acid in the stratosphere. [65]

In 1994, Prasad and Lee suggested an alternative reaction for perchloric acid formation in the stratosphere (Equation 11):



In this reaction pathway the $\text{ClO}\bullet\text{O}_3$ would be formed from the reaction of $\text{ClO}\bullet\text{O}_2$ with ozone. [66] Two years later, Jaeglé et al. [67] observed small quantities of perchlorate anion in the stratosphere as suggested by Simonailis and Heicklen [65]. The perchlorate was found in sulfate aerosols which led to a third possible mechanism for perchloric acid formation (Equation 12):



This reaction pathway is still not fully understood but it is believed to involve

the heterogeneous reaction of ClO on the surface of H₂SO₄ aerosols. [67]

In addition to the formation of perchlorate in the stratosphere by one of the three methods discussed above, alternative methods for perchlorate formation have been proposed. Atmospheric formation of perchlorate in the troposphere has been suggested. It has been proposed that ClO₂ and/or •ClO₃ may be formed in the troposphere and these compounds are converted to HClO₄ via reactions with either •OOH or •OH, respectively. [68] Studies in the laboratory using simulated atmospheric processes have shown the possibility of perchlorate formation in the atmosphere via electric discharge through NaCl aerosols. [68]

The formation of perchlorate has also been proposed at or near the Earth's surface. The formation of perchlorate from chlorine precursors at or near the Earth's surface with either UV light [69] or O₃ [70] have also been reported. Through isotopic studies of chloride and oxygen, it may be possible to constrain the mechanistic pathways.

Chloride Isotopic Analysis: Chlorine isotope analysis of the radioactive environmental isotope ³⁶Cl was performed on perchlorate samples taken from anthropogenic sources as well as natural sources from both the Atacama Desert and the southwestern United States. [71, 72] Perchlorate should exhibit a high abundance of ³⁶Cl if produced in the stratosphere because cosmogenic ³⁶Cl is formed in the stratosphere. Likewise, if the perchlorate were produced in the troposphere or at the Earth's surface, there would be a lesser abundance of ³⁶Cl because both stratospheric and marine Cl⁻, which is not enriched in ³⁶Cl, would be used in its formation. [71]

Figure 29 shows the relationship between the $\delta^{37}\text{Cl}$ to the atom ratio of $^{36}\text{Cl}/\text{Cl}$ of ClO_4^- taken from natural soil samples from the Atacama Desert in Chile and the southwestern United States as well synthetic ClO_4^- . As seen in Figure

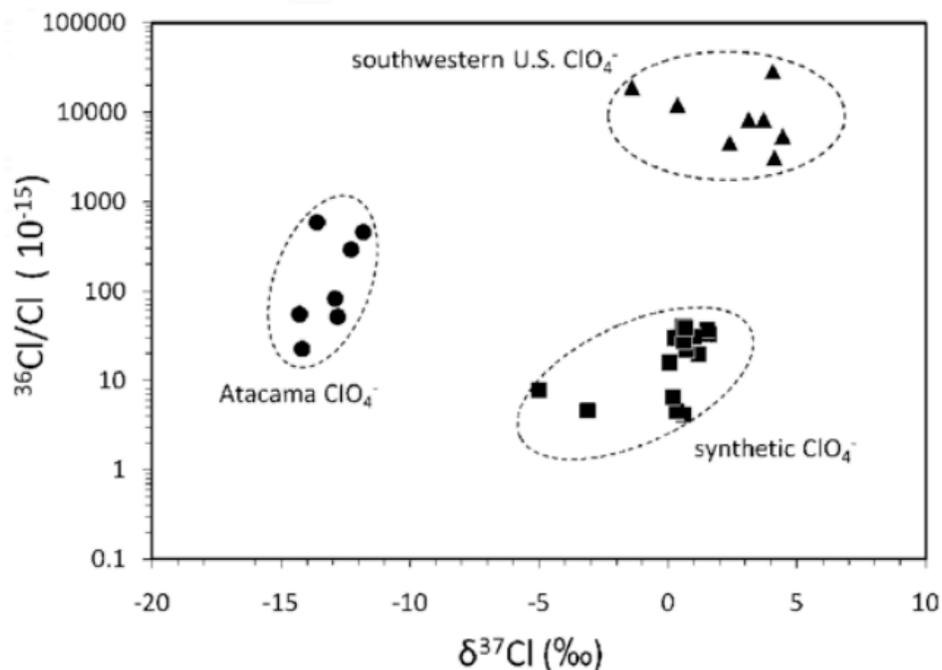


Figure 29: $^{36}\text{Cl}/\text{Cl}$ (atom ratio) versus $\delta^{37}\text{Cl}$ (permille) in samples of synthetic ClO_4^- and ClO_4^- in natural soil samples from the Atacama Desert and the southwestern United States. Adapted from [71]

29, the highest level of $^{36}\text{Cl}/\text{Cl}$ and $\delta^{37}\text{Cl}$ is found in the natural perchlorate found in the southwestern United States, while natural perchlorate from the Atacama has lower levels of both $^{36}\text{Cl}/\text{Cl}$ and $\delta^{37}\text{Cl}$, and both natural sources of perchlorate differ in $^{36}\text{Cl}/\text{Cl}$ and $\delta^{37}\text{Cl}$ from synthetic perchlorate. [71]

The higher ratio of $^{36}\text{Cl}/\text{Cl}$ in the natural perchlorate suggests it is formed in the stratosphere, not the troposphere or near land, and subsequently deposited on land. The length of time since its deposition would account for the difference in the amount of $^{36}\text{Cl}/\text{Cl}$ in the Atacama versus the southwestern United States. The half life of ^{36}Cl is 301,000a and the deposition of the perchlorate is on the order of 10^6 to 10^7 years for the Atacama and only 10^4

years for samples in the southwestern United States such as in Death Valley, California. The longer length of time the radioactive ^{36}Cl had to decay in the Atacama accounts for the lower value seen as it approaches secular equilibrium with this environment. [71, 72]

Oxygen Isotope Analysis: Bao and Gu measured the isotopic composition of perchlorate from the Atacama Desert as well as commercial sources. [73] Anthropogenic sources of perchlorate possessed $\delta^{18}\text{O}$ (*i.e.*, normalized $^{18}\text{O}/^{16}\text{O}$ ratios) at -18.4 ± 1.2 permille while natural sources valued from -4.5 to -24.8 permille. Likewise, it was found perchlorate from natural sources have a distinctly large and positive ^{17}O anomaly (or $\Delta^{17}\text{O}$). There are three possible sources of the oxygen in the perchlorate molecule: H_2O (or $\text{OH}\bullet$), O_2 from the air, or ozone. It has been found that either mass-independent oxygen isotope fractionation or isotope transfer process with atmospheric ozone resulting in the one ozone atom incorporated into the perchlorate molecule would produce the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ levels seen in natural Atacama perchlorate. [73]

The constraints placed on the mechanistic pathway from the isotopic analysis performed by Bao and Gu [73] affects the plausibility of the three formation processes in the stratosphere. The pathway from Prasad and Lee is no longer supported with this added constraint, while the pathway from Simonailis and Hecklen is still possible. The pathway from Jaeglé is still so poorly understood that it cannot be either ruled in or out.

Recently, Jackson et al. [72] extended the study of oxygen isotopic analysis of natural sources of perchlorate with the analysis of samples from the southwestern United States including samples from Texas, New Mexico and Death Valley, California. The concentration of perchlorate in Death Valley, California, ranges from 0.25 to 1.7 mg/kg, which is 1-3 orders of magnitude

lower than the concentration found in the Atacama Desert. [72]

Figure 30 shows the relationship between the $\delta^{18}\text{O}$ to the $\Delta^{17}\text{O}$ showing samples from synthetic, Atacama and Death Valley perchlorate. Combining the

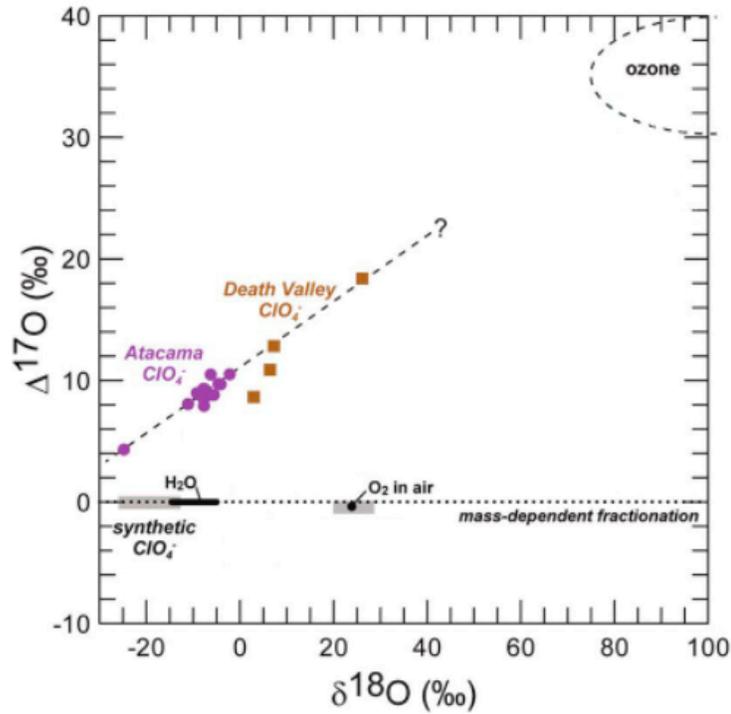


Figure 30: $\delta^{18}\text{O}$ (permille) versus $\Delta^{17}\text{O}$ (permille) in samples of synthetic ClO_4^- and ClO_4^- in natural soil samples from the Atacama Desert and Death Valley. Adapted from [72]

data from the Atacama and Death Valley, a positive correlation is seen between the $\delta^{18}\text{O}$ and the $\Delta^{17}\text{O}$. A hypothetical trend line runs from the mass-dependent fractionation line indicative of synthetic perchlorate towards the isotopic composition of atmospheric ozone. While both natural sources of perchlorate fall along this line, they both have distinctly different compositions of $\delta^{18}\text{O}$ and the $\Delta^{17}\text{O}$. The $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ are both higher in the Death Valley perchlorate than the perchlorate from the Atacama. It is possible that a difference in either formation mechanism or location of formation is responsible for the difference in the isotopic composition. A larger $\Delta^{17}\text{O}$ would suggest

stratospheric formation of perchlorate via photochemical oxidation of O_3 in which a single oxygen atom from the O_3 is transferred to the perchloric acid; while a lower $\Delta^{17}O$ would suggest that the formation occurs photochemically with another oxidation other than O_3 in the atmosphere of the formation occurs on the Earth's surface. It has been proposed that the correlation of $\delta^{18}O$ and $\Delta^{17}O$ is a mixing line between mechanisms of perchlorate formation using O_3 and mechanisms using oxidants other than O_3 , however, taken together with data of $^{36}Cl/Cl$ this may not hold true. [72]

Summary: By looking at both the chloride and oxygen isotopes in natural sources of perchlorate it is possible to distinguish natural sources of perchlorate from one another (*i.e.*, Atacama ClO_4^- from Death Valley ClO_4^-). Likewise, it is possible to use the isotopic analysis to place restraints on the possible mechanistic pathways for perchlorate formation. However, there is still no definitive pathway of perchlorate formation at the present time.

In fact, it has recently been suggested there is more than one pathway of formation leading to the presence of natural perchlorate on Earth. Studies by Furdui et al. [64] have suggested that perchlorate found in Arctic snow is the result of two different mechanisms, stratospheric chloride radical reactions with ozone which produces perchlorate year round and tropospheric perchlorate formation which produces additional perchlorate but only in the summer months.

Therefore, it is necessary to continue investigations into new locations of natural perchlorate on Earth and its isotopic composition in order to add to the overall understanding of this molecule's mechanistic formation pathway. Catling et al. [74] recently proposed using perchlorate formation in Earth's hyperarid region, specifically the Atacama Desert, as an analogy for the for-

mation of perchlorate on Mars. Thus, a better understanding of the formation of ClO_4^- on Earth could lead to the better understanding of the formation of ClO_4^- on Mars.

3.3 Experimental

Analysis of ADV Soils for Perchlorate: For analysis by ion chromatography (IC), a 1:5 weight ratio of soil to water was used for the extraction of perchlorate. This differed from the 1:25 soil to water ratio used for the extraction of all other water-soluble species discussed in Chapter 2. One gram of homogenized soil was added to 5 mL of 18.2 m Ω water. The solution was shaken for 30 seconds, leached for one hour at room temperature and then filtered through a 0.2 μm filter prior to analysis.

A Dionex ICS-2000 reagent-free ion chromatographic system (Dionex, Sunnyvale, CA, USA) was used to determine the perchlorate in leached soil solutions. The system included a dual-piston pump, a high-pressure injection valve with a 100- μl sample loop, Dionex DS6 heated conductivity cell and an AS40 automated sampler (Dionex) with which all samples were loaded. It was equipped with a Dionex Ionpac AS16 analytical column (250 x 4 mm I.D.) and an AG16 guard column (50 x 4 mm I.D.) along with an Anion Self-Generating Suppressor 300 (4-mm). The eluent was 35 mM potassium hydroxide with a flow rate of 1.25 ml/min. The data was collected and analyzed using the software package Chromeleon. These conditions were adapted from EPA Method 314.0 for the detection of perchlorate by ion chromatography. [75]

There was no internal standard added to the leachate solution for this analysis. The Dionex column (IonPac AS16) used for this analysis was specifically chosen for its ability to separate perchlorate from other interfering ions. Likewise, a program was created specifically for this analysis which allowed for a

gap of approximately eight minutes between the previously eluted ion and the perchlorate ion.

On each analysis day, a sequence was run consisting of the perchlorate calibration standards and a one milliliter aliquot of each leached soil sample. Blanks of 18.2 mΩ water were run at the beginning of the sequence after the calibration standards and at the end of the soil samples as a quality control measure. The Dionex program used ran for a total of 16.5 minutes for each sample, with 14 minutes for analysis and 2.5 minutes between samples for the autosampler to relay the solution to the IC system. All soil sample solutions were run in triplicate and were not diluted. The perchlorate standards used are listed in Table 24. All standards were prepared by dilution from a commercially available IC standard stock solution.

Table 24: IC perchlorate standards for the analysis of MDV soils

| Standard (#) | Concentration (μM) |
|-----------------|------------------------------------|
| 1 | 0.05 |
| 2 | 0.10 |
| 3 | 0.25 |
| 4 | 0.50 |
| 5 | 1.01 |
| 6 | 2.51 |

Initial IC testing was performed to determine the detection limit for perchlorate under the operating conditions discussed above. Five standard solutions were prepared from 20.11 μM down to 0.05 μM . The method detection limit (MDL) for ClO_4^- in the leachate solution was 0.05 μM (this translated to 25 $\mu\text{g}/\text{kg}$ in the soil).

3.4 Results and Discussion

Detectable levels of perchlorate ($>0.05 \mu\text{M}$ on the soil leachate or $25 \mu\text{g}/\text{kg}$ in the soil) were found in eight of the eleven ADV pits analyzed. In the stable upland zone (University and Beacon Valleys) perchlorate was present in all soil horizons from the pavement to the permafrost (Table 25). The concentration

Table 25: List of the soil samples from the stable upland zone and their corresponding concentrations of perchlorate in both the soil leachate solution (in μM) and the original soil samples (in $\mu\text{g}/\text{kg}$) when one gram of soil is leached in 5 mL of $18.2 \text{ m}\Omega$ water for one hour and analyzed by IC. The standard deviation was $<\pm 30\%$ for all measurements.

| Valley | Pit (#) | Depth (cm) | Concentration in Solution (μM) | Concentration in Soil ($\mu\text{g}/\text{kg}$) |
|------------|---------|------------|---|---|
| University | 7 | 0 | 0.33 | 166 |
| University | 7 | 5 | 1.27 | 630 |
| University | 7 | 15 | 0.49 | 244 |
| University | 7 | 25 | 0.26 | 128 |
| University | 7 | 34 | 0.20 | 100 |
| University | 10 | 0 | 0.13 | 53 |
| University | 10 | 5 | 0.18 | 91 |
| University | 10 | 15 | 0.16 | 78 |
| University | 10 | 19 | 0.06 | 31 |
| Beacon | 11 | 4 | 1.16 | 575 |
| Beacon | 11 | 25 | 0.74 | 370 |
| Beacon | 11 | 50 | 0.37 | 183 |
| Beacon | 11 | 75 | 0.34 | 167 |
| Beacon | 20 | 0 | 0.20 | 100 |
| Beacon | 20 | 2 | 0.48 | 237 |
| Beacon | 20 | 7 | 0.57 | 283 |
| Beacon | 20 | 13 | 0.09 | 44 |
| Beacon | 20 | 19 | 0.09 | 44 |

of ClO_4^- in these soils ranged from 0.06 to $1.27 \mu\text{M}$ in the soil leachate solution (or 31 to $630 \mu\text{g}/\text{kg}$ in soil) in University Valley and 0.09 to $1.16 \mu\text{M}$ in the soil leachate solution (or 44 to $575 \mu\text{g}/\text{kg}$ in soil) in Beacon Valley. Figure 31 shows the perchlorate versus depth profile for the University and Beacon Valley soils. While perchlorate was ubiquitous in the stable upland zone, this was not the

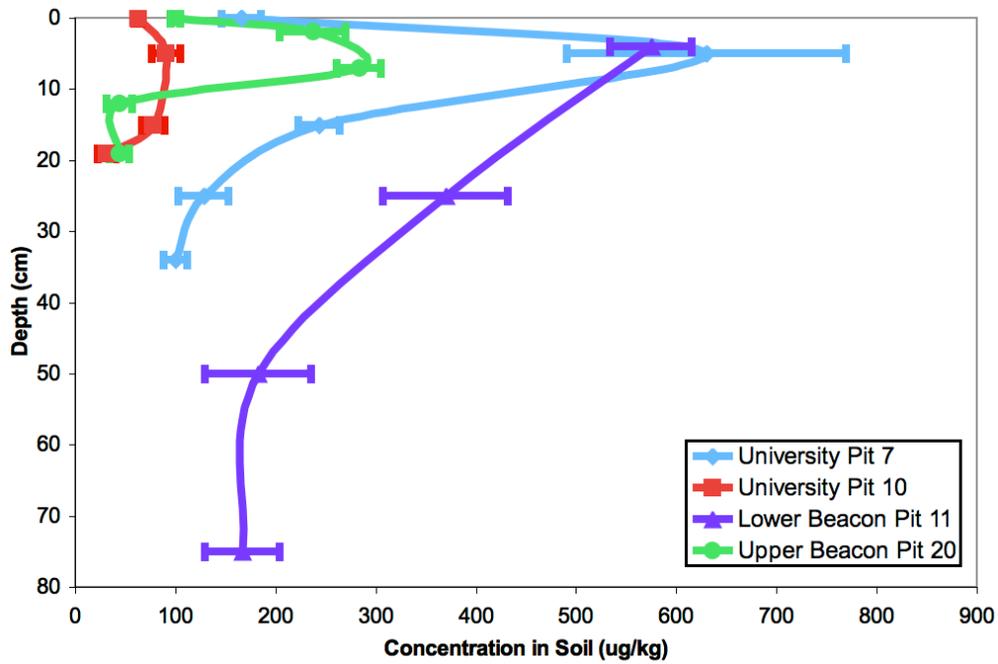


Figure 31: Plot of the concentration of perchlorate in the soils from the stable upland zone (in $\mu\text{g}/\text{kg}$), when one gram of soil is leached in 5 mL of 18.2 m Ω water for one hour and analyzed by IC, as a function of depth (in cm). [76]

case in the inland mixed zone and coastal thaw zone. Perchlorate was below the instrument's detection limit of 0.05 μM on the soil leachate (or 25 $\mu\text{g}/\text{kg}$ in the soil) in the pit dug in Wright Valley as well as in all but one soil horizon in Victoria Valley where ClO_4^- was measured at a concentration of 0.12 μM in the soil leachate solution (or 62 $\mu\text{g}/\text{kg}$ in the soil). In Taylor Valley, 6 of the 23 soil horizons sampled measured detectable levels of perchlorate ranging from 0.10 to a high of 2.22 μM ClO_4^- in the soil leachate solution (or 52 to 1103 $\mu\text{g}/\text{kg}$ in the soil). There was no regular or discernible pattern to the presence of perchlorate in this valley. [76]

The presence of perchlorate in all soil horizons of all soil samples collected from the valleys in the stable upland zone was the result of the below freezing temperatures and hyper-arid conditions which inhibit long range aqueous ion migration of this highly soluble salt. In contrast, the low and highly variable

concentrations of perchlorate in the inland mixed zone and coastal thaw zone (Table 26) can be attributed to the moderate climate of these zones. The

Table 26: List of soil samples from the coastal thaw zone and inland mixed zone and their corresponding concentrations of perchlorate in both the soil leachate solution (in μM) and the original soil samples (in $\mu\text{g}/\text{kg}$) when one gram of soil is leached in 5 mL of 18.2 m Ω water for one hour and analyzed by IC. The standard deviation was $<\pm 175\%$ for all measurements.

| Valley | Pit (#) | Depth (cm) | Concentration in Solution (μM) | Concentration in Soil ($\mu\text{g}/\text{kg}$) |
|----------|---------|------------|---|---|
| Taylor | 1 | 0 | 0.22 | 109 |
| Taylor | 1 | 4 | 0.18 | 92 |
| Taylor | 1 | 18 | 0.09 | 47 |
| Taylor | 2 | 15 | 2.22 | 1103 |
| Taylor | 2 | 28 | 0.57 | 286 |
| Taylor | 3 | 4 | 0.10 | 52 |
| Victoria | 9 | 8 | 0.12 | 62 |

warmer temperatures, higher moisture content and more meltwater allow for the migration of perchlorate to inaccessible locations or eventually into the ocean. [76]

Perchlorate Correlation to Other Anions: As discussed in Chapter 2, the most abundant anions present in the MDV were: Cl^- , NO_3^- , and SO_4^{2-} . The concentration of perchlorate in the soil (in $\mu\text{g}/\text{kg}$) was plotted versus the concentration of Cl^- , NO_3^- , and SO_4^{2-} in the soil (in mg/kg) in the stable upland zone and the coastal thaw zone. The inland mixed zone was excluded since there was only one perchlorate data point for this zone. Correlation between perchlorate and another anion suggests both anions share a common depositional and evapoconcentrated source.

Both Cl^- [77] and NO_3^- [25] are atmospherically deposited. Any correlation of these ions with ClO_4^- would strengthen the argument for ClO_4^- atmospheric formation. Concentrations of chloride ranged from 9.67 μM to

3.46 mM in the soil leachate solution (or 9 to 3062 mg/kg in the soil) in the coastal thaw zone and from 0.19 to 3.02 mM in the soil leachate solution (or 166 to 2680 mg/kg in the soil) in the stable upland zone. Concentrations of nitrate ranged from not detected to 0.23 mM in the soil leachate solution (or not detected to 358 mg/kg in the soil) in the coastal thaw zone and from 0.36 to 2.90 mM in the soil leachate solution (or 551 to 4488 mg/kg in the soil) in the stable upland zone. As with sulfate, the concentrations of chloride and nitrate are several orders of magnitude higher than the concentrations of perchlorate in all zones.

Figure 32 shows the plots for Cl^- versus ClO_4^- and NO_3^- versus ClO_4^- from the four different pits in the stable upland zone. There was a high correlation between $[\text{ClO}_4^-]$ and both $[\text{Cl}^-]$ ($R^2 = 0.6535$) and $[\text{NO}_3^-]$ ($R^2 = 0.7504$) in the coastal thaw zone when all soils points were plotted for all four pits, and the correlation improved ($R^2 = 0.8493$ and 0.8523 , respectively) when plotting only the data containing detectable amounts of ClO_4^- . There was also a high correlation between $[\text{ClO}_4^-]$ and $[\text{Cl}^-]$ in the each pit on the stable upland zone (with $R^2 = 0.9780$ in Pit 7, 0.6956 in Pit 10, 0.9383 in Pit 11 and 0.7876 in Pit 20) and $[\text{NO}_3^-]$ in each pit in the stable upland zone (with $R^2 = 0.8536$ in Pit 7, 0.8881 in Pit 10, 0.9556 in Pit 11 and 0.9309 in Pit 20).

The concentration of sulfate ranged from $3.46 \mu\text{M}$ to 0.39 mM in the soil leachate solution (or 8 to 934 mg/kg in the soil) in the coastal thaw zone and 0.26 to 9.17 mM in the soil leachate solution (or 619 to 22005 mg/kg in the soil) in the stable upland zone. Thus, the $[\text{SO}_4^{2-}]$ is several orders of magnitude higher than the $[\text{ClO}_4^-]$ in both zones. In the global sulfur cycle, sulfate is produced atmospherically by the oxidation of gas and aqueous phase S(IV) species such as SO_2 , $\text{SO}_2 \bullet \text{H}_2\text{O}$, HSO_3^- , and SO_3^{2-} . The sulfate

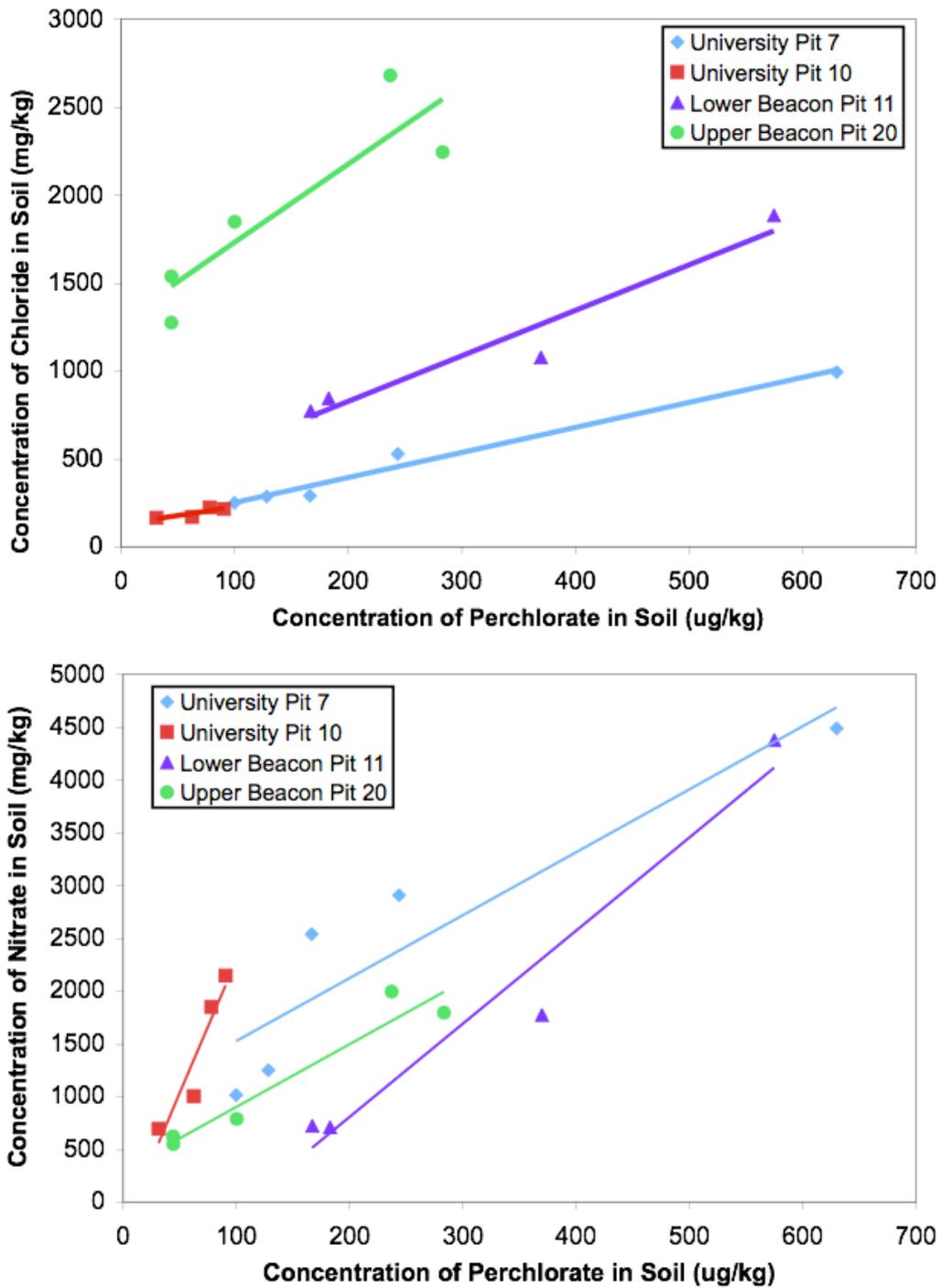


Figure 32: Correlation of perchlorate to other anions in the stable upland zone: chloride (top) and nitrate (bottom). [76]

then precipitates onto land where it accumulates in the soil. [25, 73, 78] As previously discussed, it is widely believed that perchlorate is also formed in the atmosphere. Therefore, if the only source of sulfate in the McMurdo Dry Valleys comes from atmospheric deposition these two ions should be highly correlated.

In the coastal thaw zone, $[\text{ClO}_4^-]$ does not correlate with $[\text{SO}_4^{2-}]$ when plotting all data points ($R^2 = 0.0048$) or when plotting only data points for which ClO_4^- is detectable ($R^2 = 0.0513$). However, when $[\text{ClO}_4^-]$ is plotted versus $[\text{SO}_4^{2-}]$ for each of the four pits in the stable upland zone there is high correlation in each pit ($R^2 = 0.7389$ in Pit 7, 0.9042 in Pit 10, 0.8010 in Pit 11 and 0.7899 in Pit 20). However, the correlations are not as high when the data for both pits in the same valley are plotted jointly ($R^2 = 0.3458$ in University Valley and 0.5878 in Beacon Valley) and are not at all correlated when all pits from the stable upland zone are plotted jointly ($R^2 = 0.1271$). The lack of significant correlation between these two ions in the coastal thaw zone does not necessarily suggest the perchlorate was not formed atmospherically, rather it suggests there were other sources contributing to the concentrations of either sulfate or perchlorate in this zone. In fact, it is known that a significant source of sulfate in the MDV comes from the ocean. NaSO_4 from the ocean is transported to the coastal thaw zone via marine aerosols. [35] This additional input of marine SO_4^- could account for the lack of correlation between the two ions in this zone. Likewise, in the stable upland zone the correlations hold best within a single pit and not within the valley or the microclimate zone as a whole. This suggests that while the deposition source may be the same for both ions, the distribution of these ions varies greatly by location.

Perchlorate Formation Pathway: The discovery of yet another natural source of perchlorate on Earth, in the McMurdo Dry Valley of Antarctica, could help further constrain the possible pathways for this compound's formation. Currently, soil from MDV has been sent out for isotopic analysis. However, it may prove difficult to obtain enough perchlorate to perform isotopic analysis due to the small concentration present in these soils. Since there is yet to be any isotopic analysis performed on the perchlorate from the soils in the MDV, it is not yet possible to further constrain the possible mechanism for the formation pathway. However, it is possible to speculate on the perceived possible isotopic composition of these soils compared to perchlorate in other arid regions, such as Death Valley and the Atacama.

The $^{36}\text{Cl}/\text{Cl}$ ratio seen in perchlorate is high in the samples taken from Death Valley and the soils in the southwestern United States, while the ratio is lower for samples in the Atacama approaching the ratio seen in anthropogenic perchlorate. [71] Since it is believed that the difference in $^{36}\text{Cl}/\text{Cl}$ ratio is the result of the time elapsed since deposition, with decreased $^{36}\text{Cl}/\text{Cl}$ ratio with increased time since deposition, the perchlorate in the McMurdo Dry Valleys would have an even lower $^{36}\text{Cl}/\text{Cl}$ ratio due to the increased age of the soil. Likewise, the ratio would be lower for perchlorate in the older aged stable upper zone soil than the coastal thaw zone soils and would decrease with soil depth as well. In fact, the values would likely be approaching secular equilibrium with the environment.

The reasoning behind the difference in the $\delta^{37}\text{Cl}$ values in the Atacama and Death Valley perchlorate is unknown due to a lack of data. Therefore, it is not certain where the $\delta^{37}\text{Cl}$ values would lie compared to the values for perchlorate from the other two environments. As for the isotopic oxygen composition in the perchlorate from the McMurdo Dry Valleys, it would be reasonable to

assume the these soils would lie along the same correlation line as the samples from the Atacama and Death Valley (see Figure 30). However, where on the line this data would fall is still unknown.

3.5 Conclusions

The discovery of perchlorate in the McMurdo Dry Valleys of Antarctica has helped to strengthen the argument that this compound is ubiquitous on Earth and accumulates only in hyperarid regions where its rate of deposition exceed the rate of dissolution. Likewise, it has been shown that while the overall highest $[\text{ClO}_4^-]$, $2.22\mu\text{M}$ in the soil leachate solution (or $1103\ \mu\text{g}/\text{kg}$ in the soil), was found in a single soil horizon in a pit dug in the coastal thaw zone, ClO_4 was found consistently at high concentrations in all soil horizons of the stable upland zone, the most arid of the three microclimate zones, ranging in concentration from 0.06 to $1.27\ \mu\text{M}$ in the soil leachate solution (or 31 to $630\ \mu\text{g}/\text{kg}$ in the soil).

The concentration of perchlorate was highly correlated with $[\text{Cl}^-]$, $[\text{NO}_3^-]$ and $[\text{SO}_4^{2-}]$ in each pit from the stable upland zone even though these ions were present at orders of magnitude higher concentrations. Correlations also existed between $[\text{Cl}^-]$ and $[\text{ClO}_4^-]$ and $[\text{NO}_3^-]$ and $[\text{ClO}_4^-]$ in the coastal thaw zone. The correlation of $[\text{SO}_4^{2-}]$, $[\text{Cl}^-]$ and $[\text{NO}_3^-]$ with $[\text{ClO}_4^-]$ strengthens the argument of an atmospheric formation pathway.

However, only speculation of the isotopic composition may be made at this time until isotopic analysis can be performed. Without isotopic analysis of perchlorate from these soils, it is not possible to put any further constraints on the possible mechanism of formation at the present time. Therefore more analysis, including isotopic analysis, needs to be performed on soil samples from various arid and hyperarid regions on Earth to further the understand-

ing of perchlorate formation on Earth. By furthering the understanding of perchlorate formation and deposition on Earth, it will also help in furthering the understanding of the high levels of perchlorate found on Mars.

4 Analysis of Soils from the Atacama Desert

4.1 Introduction

The Atacama is considered by some to be one of the best Mars analog environment on Earth. The soils in the Atacama Desert physically resemble the surface of Mars and have been found to be pH neutral, oxidizing, and saline. [79, 80] Due to the aridity of the region, the soils have accumulated high concentrations of nitrate, sulfate, chloride, and perchlorate. [80, 81] For many years, it has been proposed the Atacama Desert and Mars have similar concentrations of these ions. [81] Additionally, due to the extreme aridity, the soils of the Atacama Desert are considered valuable in their ability to provide information as to how life can survive in conditions without water. [80] For these reasons, many scientists use this extreme environment for the testing of next generation instruments for Mars exploration. [82, 83, 84]

This chapter provides a background of the physical characteristics of the Atacama Desert in Chile followed by the experimental parameters for the analysis of these soils to determine pH, electrical conductivity, ionic strength and soluble ionic species. The results of this analysis are discussed. Then the soils from this extreme environment are compared to the soils of another extreme environment: the north polar region of Mars.

4.2 Background

The Atacama Desert is located on a plateau on the northern Pacific coast of Chile in South America (from 30 °S to 20 °S latitude). It measures 1,000 km long and only a few hundred km wide (Figure 33). [85, 86, 87] The average air temperature in the Atacama is ~ 16.5 °C with a maximum temperature of ~ 37 °C and a minimum of ~ -6 °C. These cooler temperatures are due to

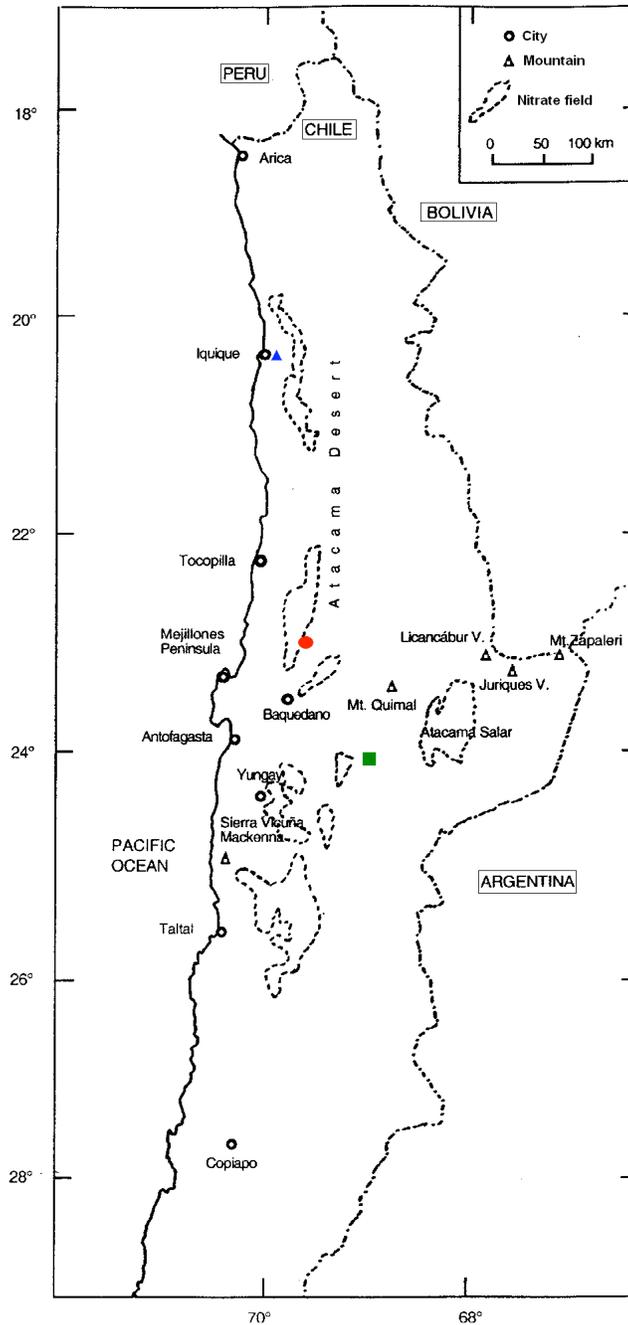


Figure 33: Map of the Atacama Desert, Chile. The blue triangle, red circle and green square mark the approximate locations of the sampling sites discussed in this work: transect AT10 P, pit AT10 OE and pit AT10 6, respectively. Adapted from Figure 1 in [24].

its proximity to the Pacific Ocean and classify the Atacama as a temperate desert. [86, 87] While temperate in temperature, the Atacama is the driest and most arid desert on Earth with less than two millimeters of rainfall a year [81] (although during El Niño in 1997, there was a recorded 2.3 mm of rain in the month of May [87]), with the driest portion located between $\sim 22^\circ\text{S}$ to 26°S . [86, 87]

Salt Accumulation: Some of the largest deposits of salts in the Atacama are found in the numerous salars.¹⁰ Salar are found across Bolivia, Chile and Argentina in the Central Andes of South America. The largest salar in Chile and second largest in the world, the Salar de Atacama, is located in the Atacama Desert, 160 km east of Antofagasta. This salar measures a surface area of nearly 3,000 km². [88, 89, 90] The main evaporitic body of this salar, the ‘salar nucleus,’ is dominated with halite (NaCl) measuring ~ 1.1 km² in area and $\sim 1,000$ m in thickness. In addition to Na⁺ and Cl⁻, other major ions include: Li⁺, K⁺, Mg²⁺, Ca²⁺, B, HCO₃⁻, and SO₄²⁻. [88, 89, 90] Minor and trace elements of, Al, As, Ba, Cd, Cu, Fe, Mn, Ni, P, Pb, Rb, Si, Sr, V, and Zn are also present in this salar. [89] There are many other smaller salars in the Atacama, all with soluble salts similar to those present in the Salar de Atacama. [91, 92]

Another large concentration of salts in the Atacama are found in Chilean salt deposits called caliche.¹¹ Caliche is found in the northern Chilean provinces of Tarapaca and Antofagasta (from $19^\circ 30'$ to 26° S latitude) at altitudes of 1,000-2,000 meters. [93] The deposits run north to south roughly 700 km in length measuring from a few kilometers wide to several tens of kilometers wide for a total surface area of $\sim 21,000$ km². [93, 94, 95] The caliche itself

¹⁰A definition of salar can be found in Appendix B

¹¹A definition of caliche can be found in Appendix B

can measure from a few centimeters to 1.2 to 1.5 meters or more. [96] Soluble species present in these deposits include: sodium nitrate (NaNO_3), potassium nitrate (KNO_3), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), calcium sulfate (CaSO_4), and magnesium sulfate (MgSO_4), as well as IO_3^- , ClO_3^- , ClO_4^- , $\text{B}(\text{OH})_4^-$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, and BO_3^{3-} . [93, 94, 95, 96] One theory for the formation of these deposits is through capillary circulation in which underground, highly saline waters from the summits of the Andes at one time circulated very slowly to the desert surface where the water evaporated rapidly leaving behind large quantities of salts. [96] Though their origin is still not certain, these deposits have been known since 1809 and have been mined and exported to North America for use as fertilizers since 1830. [96]

As seen from the presence of salars and caliche deposits, the limited precipitation and water activity in the Atacama Desert allows for the accumulation of salts in this hyperarid environment. A wide variety of soluble ions have been identified in the soils from the Atacama Desert including: Li^+ , Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , HCO_3^- , IO_3^- , ClO_3^- , ClO_4^- , $\text{B}(\text{OH})_4^-$, SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, and BO_3^{3-} . [25, 73, 77, 81, 93, 94, 95, 97]. Proposed origins for the salts present in the Atacama Desert can be divided into five main categories: atmospheric sources, oceanic sources, wind erosion, volcanic emissions and weathering.

A flow chart with possible pathways for the origins of salts in the Atacama Desert is shown in Figure 34. Atmospheric deposition brings anions, many of which are formed in the stratosphere, to the Desert including: Cl^- , NO_3^- , ClO_4^- , and SO_4^- . [25, 73, 77] The Pacific Ocean also brings many ions to the Desert in the form of nitrates, NaCl , $\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$, and $[\text{Mg}(\text{Ca})]\text{SO}_4 \cdot 2\text{H}_2\text{O}$, via sea spray, marine aerosols and fog. [25, 73, 77, 97] Weathering of different materials is another large source of the salts in the Atacama, including Ca^{2+}

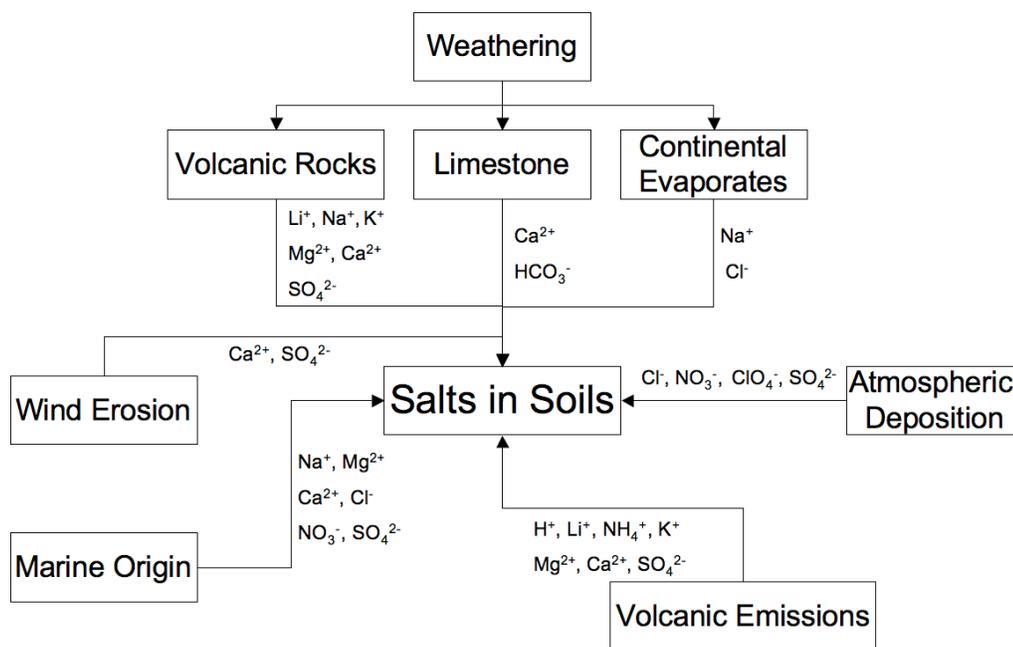


Figure 34: Pathways of Salt Accumulation in the Soils of the Atacama Desert

and CO_3^{2-} from limestone, NaCl from continental evaporites, and Li^+ , K^+ , Mg^{2+} and B , and to a lesser extent Na^+ and Ca^{2+} , from volcanic rocks. [88, 97] Wind erosion is also believed to be a source of CaSO_4 , as is direct volcanic emissions which also provides other sulfates including H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$. [97] The fluid of volcanic emissions is also a source of Li^+ , K^+ , Mg^{2+} and B . [88] Thus, the salts in the Atacama Desert of Chile appear to consist mainly of the anions: Cl^- , NO_3^- , ClO_4^- and SO_4^{2-} and the cations: Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+} , which are similar to the main ions found in the McMurdo Dry Valleys of Antarctica (see Chapter 2) and the soils of the north polar region of Mars (see Chapter 1).

Similarities Between Atacama and Mars: There are several characteristics which make the soil from the Atacama a suitable analog for the soil on Mars. The soil in the Atacama is very dry (50 times drier than other arid and

hyperarid regions [45]) and very old (up to 2 million years [44]). Like Mars and the MDV, the Atacama also exhibits patterned ground. However, the process which forms these polygons is different than the process of polygon formation in the MDV. These polygons are formed when salt minerals cement soil grains to create the cohesion necessary to form contraction cracks. The cracks are subsequently filled with sand and sediment to present their closure. Repeated salt mineral dissolution/precipitation and thermal expansion/contraction over many years result in the patterned ground seen in the Atacama and other warm arid deserts. [98] While the polygons in the north polar region of Mars are believed to form by the same processes as the MDV polygons (*i.e.* frost heave processes [34]), there are also polygons closer to the equator on Mars which may result from the salt heave processes which form the Atacama Desert polygons. [98]

The soils in the Atacama are also filled with soluble salts similar to those found on Mars. Most notably, the Atacama contains 0.03 to 0.6 wt. % perchlorate [44], the highest concentration of natural perchlorate found on Earth to date, which is similar in concentration on the high end to the 0.6 wt. % perchlorate recently found on Mars by the Phoenix Mars Lander [19] The soils in the Atacama have low levels of organic material (0.026 to 0.056 wt. % in the Yungay Region [45]) and soil bacteria [44] whereas there has yet to be any verification of organics or bacteria on Mars. Additionally, Mars is bombarded with intense levels of radiation and the soil is believed to be oxidizing, while the Atacama is also known to exhibit oxidizing soil chemistry. [45]

Despite the many similarities between the Atacama Desert and the present day conditions on Mars there is a very evident difference between these two environments, temperature. While Mars temperatures are very frigid ranging from -123 to 25 °C on the surface [45], the Atacama is a moderate desert with

a temperature range of roughly 6 to 27 °C [86, 87]. Another difference, which arises from the vast difference in temperature between these two environments, is the lack of any dry permafrost or subsurface ice in the Atacama. Despite these differences, soils from the Atacama are still widely used for the testing of novel Mars instrumentation (such as the Sample Analysis at Mars [82] and the Urey [83]) and for the re-evaluation of experiments performed on the surface of Mars (such as a re-analysis of the Viking results [84]).

4.3 Experimental

4.3.1 Collection of Atacama Soils

Soils samples were collected from two locations within the Antofagasta Region near the town of Antofagasta, Chile. The first location was in the Oficina Ercilla Valley at 23°8.6'S, 69.51°59.7'W by a salt mine (approximate location shown in Figure 33: red circle marker). A pit, AT10 OE, was dug to a depth of 250 cm and 26 samples were collected in 10 cm intervals (for a complete list see Appendix F). The second location was located at 24°5.29'S, 69°59.67'W off the roadway (approximate location shown in Figure 33: green square marker). A pit, AT10 6, was dug to a depth of 170 cm, reaching a layer of caliche blanco.¹² A total of 12 soil samples were collected in 15 cm depth intervals (for a complete list see Appendix F). A sample of the caliche blanco was also collected. A subset of the bulk soil and caliche blanco collected by Dr. Mark Claire from the University of Washington was sent to Tufts University for analysis.

Soil samples were also collected from a location within the Tarapacá Region near the town of Iquique, Chile. Exact GPS coordinates are not available; however, it is known the samples were collected near the 40 km marker of Chile

¹²A definition of caliche blanco can be found in Appendix B

Route 16: the road to Iquique from the Pan-American Highway (approximate location shown in Figure 33: blue triangle marker). Instead of a pit, a linear transect of soils, AT10 P, was collected. A sample of soil from the top-most soil, down ~ 1 cm, was collected every meter for 9 meters. Additional soils, from the top-most soil down ~ 1 cm, were collected every 10 centimeters between meters 4 and 5 for a total of 18 samples (for a complete list see Appendix F). A subset of the bulk soil collected by Dr. Mark Claire from the University of Washington was sent to Tufts University for analysis.

4.3.2 Soil Preparation

Each soil sample was sieved to remove particles larger than 2 mm in size. The >2 mm portion was then examined for loosely bound soil clumps. Any soil clumps were transferred to a mortar and gently tapped with a pestle to break them apart. This portion was then re-sieved and the <2 mm portions were combined. Soil samples were then prepared further depending on the method of analysis.

4.3.3 Soluble Ion Analysis

Soil samples from the Atacama Desert were analyzed for a variety of water-soluble species. Soil samples from three locations throughout the Atacama (see Figure 33) were analyzed for Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , Br^- , ClO_4^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} by ion chromatography (IC) and CO_3^{2-} and HCO_3^- by acid-base titration. A subset of these soils, 5 from each location, were also analyzed for Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , NO_3^- , and SO_4^{2-} using the ion selective electrodes (ISEs) in the wet chemistry laboratory (WCL) testbeds designed for the analysis of the Martian soil during the Phoenix Mars mission (see Chapter 1). Additionally, some

slightly different methods were necessary to analyze the caliche blanco sample collected from AT10 6. Each method of soluble ion analysis, including any additional soil preparation associated with that analysis is discussed below.

Ion Chromatography Procedure: For analysis by ion chromatography (IC), further soil sample preparation was necessary. A 1:5 weight ratio of soil to water was used for the extraction of soluble ionic species. One gram of the <2 mm soil was added to five milliliters of 18.2 m Ω water. The solution was shaken for 30 seconds and leached for one hour at room temperature. The solution was filtered through a 0.2 μ m filter prior to analysis. The leached solution was stored in a tightly sealed glass vial on the bench-top until analyzed. After as little as 24 hours, needle-like salt crystals were discovered at the bottom of the glass vial in several of the leachate solutions from AT10 6 and AT10 OE. Therefore, it was necessary to perform any analysis on the soil leachate within hours of filtration.

Soluble ions in the Atacama soil leachates were determined by the same methods used for the analysis of soils from the McMurdo Dry Valleys. Ion chromatography was used to determine the cationic and anionic water-soluble species present. The cationic species: Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺ and Ba²⁺ and anionic species: Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, and PO₄³⁻ were analyzed following the procedure for IC analysis outlined in Chapter 2 using the cation and standards listed in Tables 27 and 28 . The leached samples were diluted 1000-fold prior to analysis and the samples were run in triplicate. A subset of the samples, which had a substantial amount of sulfate, were diluted an additional 50-fold, for a total dilution of 50,000-fold and re-run in triplicate to determine the amount of SO₄²⁻ in the sample. The amount of all other ions was determined from the 1000-fold dilution.

Table 27: IC cation standards for the analysis of Atacama Desert soils

| | Standard 1 | Standard 2 | Standard 3 |
|------------------|-------------------|-------------------|-------------------|
| Cation | (μM) | (μM) | (μM) |
| Li^+ | 14.4 | 72.0 | 1440.7 |
| Na^+ | 17.4 | 87.0 | 1739.9 |
| NH_4^+ | 27.7 | 138.6 | 2771.9 |
| K^+ | 25.6 | 127.9 | 2557.7 |
| Mg^{2+} | 20.8 | 104.0 | 2080.7 |
| Ca^{2+} | 25.0 | 124.8 | 2495.1 |
| Ba^{2+} | 7.3 | 36.4 | 182.0 |

Table 28: IC anion standards for the analysis of Atacama Desert soils

| | Standard 4 | Standard 5 | Standard 6 |
|--------------------|-------------------|-------------------|-------------------|
| Anion | (μM) | (μM) | (μM) |
| Cl^- | 2.8 | 11.3 | 282.1 |
| Br^- | 2.5 | 10.0 | 250.3 |
| NO_3^- | 2.1 | 8.3 | 208.2 |
| SO_4^{2-} | 3.2 | 12.9 | 322.6 |
| PO_4^{3-} | 3.2 | 12.6 | 315.9 |

The samples were also analyzed by IC for the presence of perchlorate. The procedure for perchlorate analysis by IC is outlined in Chapter 3. Table 29 lists the concentrations of the perchlorate standards used for this analysis. The soil leachate solutions were run in triplicate with no dilution.

Table 29: IC perchlorate standards for the analysis of Atacama soils

| Standard | Concentration |
|----------|-------------------|
| (#) | (μM) |
| 1 | 0.05 |
| 2 | 0.10 |
| 3 | 0.25 |
| 4 | 0.50 |
| 5 | 1.01 |
| 6 | 2.51 |

Acid-Base Titration Procedure: The presence or absence and concentration of two other water-soluble species, CO_3^{2-} and HCO_3^- , were also de-

terminated by acid-base titration with a standardized H_2SO_4 solution. The procedure for this analysis is identical to the procedure discussed in Chapter 2 for the titration of McMurdo Dry Valley (MDV) soils. The only difference in the analysis was the soil to water ratio. Instead of a 1:25 weight ratio of soil to water used in the analysis of MDV soils, a 1:10 weight ratio of soil to water (5 grams of soil in 50 mL of 18.2 m Ω water) was chosen. The use of a 1:10 weight ratio was chosen over a 1:5 weight ratio used for the analysis of all other soluble ions, by WCL and IC, due to limited soil availability.

Wet Chemistry Laboratory Procedure: For analysis in a WCL testbed (see Figure 2 in Chapter 1), no further soil sample preparation was necessary. At the start of each new day of analysis the testbed was removed from the refrigerator and 25 mL of TS20 was added to the cell to re-hydrate the ISEs for a minimum of one hour prior to analysis. Table 2 in Chapter 1, lists the composition of TS20. The WCL testbed was then calibrated using the spiking method discussed in Chapter 1.

After calibration, the testbed was rinsed three times with 18.2 m Ω water and once with TS20 before being filled again with 25 mL of TS20. The stirrer and sensors were turned on and data was collected for 10 minutes which allowed time for the solution to equilibrate. Then the solution was spiked to TS21. Once the solution equilibrated and data was collected for five minutes, a 1 cm³ scoop was used to transfer 1 cm³ of soil to the cell. The data was collected for a total of one hour from the time of soil addition. After one hour, the stirrer and sensors were turned off. If more than one sample was run per day, the testbed was rinsed thoroughly with 18.2 m Ω to remove all soil, then rinsed once with TS20 before 25 mL of TS20 was added and the process was repeated. All data collection for both calibrations and samples was performed

in a laptop computer using customized LabView software.

Analysis of the Caliche Blanco: The caliche blanco sample taken at a depth of 170+ cm from AT10 6 could not be analyzed for anions and cations by IC due to the extremely high salt content (close to 100%). However, it was possible to analyze this sample for perchlorate by IC due to the differences in the instrument's experimental set-up. Several other tests were performed to gather some additional information about more of the soluble species present in this sample. To determine the approximate concentrations of NO_3^- and SO_4^{2-} in the sample, test strips designed for identification and semi-quantitative detection of NO_3^- (EM Quant $\text{\textcircled{R}}$) and SO_4^{2-} (Quantofix $\text{\textcircled{R}}$) were used according the instructions on the package. Finally, several of the salt crystals from the caliche blanco sample were examined using a scanning electron microscope equipped with energy-dispersive x-ray spectroscopy (SEM-EDX) to determine their chemical composition looking specifically for water-soluble species.

4.3.4 pH, Conductivity and Ionic Strength Analysis

In addition to the analysis of soil for water-soluble ions, the soil leachate solutions were also analyzed for pH, conductivity, and ionic strength. As with the IC analysis, further soil preparation was necessary. A 1:5 weight ratio of soil to water was used to for the extraction of soluble ionic species. One gram of the < 2-mm soil was added to 5 mL of 18.2 m Ω water. The solution was shaken for 30 seconds and leached for one hour at room temperature. The solution was filtered through a 0.2 μm filter prior to analysis. The leached solution was stored in a tightly sealed glass vial on the bench-top until analyzed. Further details of each analysis are discussed below.

pH: The pH of all Atacama soil leachate was determined by measurement with a commercial pH probe (Thermo Fisher Scientific ORION 3-Star pH Meter). Measurements were taken in triplicate at room temperature. The pH probe was calibrated with pH 4, 7, and 10 buffers prior to analysis. The pH measurements were performed within hours of filtering the soil leachate before any potential precipitate formed which could alter this measurement.

Solution Electrical Conductivity: The total conductivity of all Atacama soil leachates was determined by measurement with a commercial conductivity probe (Orion). Measurements were taken in triplicate at room temperature. The conductivity probe was calibrated prior to analysis with solutions of 100 $\mu\text{S}/\text{cm}$, 1413 $\mu\text{S}/\text{cm}$ and 12.9 mS/cm KCl. The conductivity measurements were performed within hours of filtering the soil leachate before any potential precipitate formed which could alter this measurement.

Ionic Strength: As with the soils from the McMurdo Dry Valleys (Chapter 2) the ionic strength (μ) was calculated for each soil sample using two separate methods: using the IC and acid-base titration data (Equation 7) and using the measured electrical conductivity (Equation 8). Ideally, if all ions present in the leached soil solutions were identified and quantified by the IC, the results of Equations 7 and 8 should be identical. However, iodate (IO_3^-) has previously been found in Atacama soils in substantial amounts in the nitrate ores. [25]. IO_3^- is another anion, like ClO_4^- , which requires a specialized IC set-up and therefore was not specifically analyzed for in this analysis. Therefore, it was expected the μ_{exp} calculated from Equation 8 would be greater than the μ_m calculated from Equation 7.

4.3.5 Analysis of the Unknown Precipitate

After as little as 24 hours, a precipitate formed in some of the glass vials used to store the leachate solution for samples from AT10 6 and AT10 OE. To determine the composition of the precipitate, the leachate solution was decanted from the storage vials allowing only the crystals on the bottom to remain. Once the vial was completely dry the crystals were removed from the vials and analyzed under a scanning electron microscope equipped with energy-dispersive x-ray spectroscopy (SEM-EDX) to determine the crystal's chemical composition. Several crystals from various soil leachates were examined to confirm the precipitate crystal's were consistent in composition.

4.4 Results and Discussion

Soil samples from the Atacama Desert were analyzed for a variety of water-soluble species, by ion chromatography (IC), acid-base titration, and the ion selective electrodes (ISEs) in the wet chemistry laboratory (WCL). Additionally, the pH, conductivity and ionic strength of the soil samples were also determined. Results from these analyses will be discussed along with a comparison to other soils previously analyzed from the Atacama. This will be followed by a comparison of soils from the linear transect location, AT10 P, to the soil from the northern polar region of Mars at the Phoenix landing site (Chapter 1).

4.4.1 Soluble Ions

Soil samples from three locations throughout the Atacama Desert (Figure 33) were analyzed by ion chromatography (IC) and acid-base titration for a variety of water-soluble species. IC was chosen as the method of choice for soluble ion analysis because it is capable of detecting a wide range of

anions and cations allowing for a more complete analysis. The IC analysis was supplemented with acid-base titration for the detection and quantification of carbonate and bicarbonate due to the difficulty of quantifying these species with IC. A discussion of the results is divided by location: AT10 OE, AT10 6, and AT10 P.

In addition, a subset of soils from each location were also analyzed for soluble ions by the ISEs in the WCL, the instrument which preformed the analysis of the Martian soil (see Chapter 1). WCL analysis is limited to the detection and quantification of only nine ions: Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , and $\text{NO}_3^-/\text{ClO}_4^-$. Though a less thorough method of analyzing for soluble ions, the WCL analysis was preformed on a subset of soils in order to provide a complimentary analysis technique and help create a catalog of WCL responses to a variety of Mars analog soils. The WCL results are discussed along with a comparison of the WCL and IC data.

Ion Chromatography and Acid-Base Titration Results: Ion chromatography was used to determine the water-soluble ionic species present in the soils from two pits at locations AT10 and AT10 OE and a linear transect of the top-soil at the location AT10 P collected from the Atacama Desert. Additionally, acid-base titrations were also performed to determine the concentrations of carbonate and bicarbonate in the soils which could not be quantified by IC. Tables listing the concentration of each soluble ion in each soil leachate solution (in μM and/or mM) and original soil sample (in $\mu\text{g}/\text{kg}$ and/or mg/kg) can be found in Appendix G. Separate techniques were used to look at the sample of caliche blanco in AT10 6. The three sampling areas were spread out across the Atacama (Figure 33). Thus each location will be discussed separately.

AT10 OE: Twenty-five soil samples were collected at 10 cm intervals in depth from AT10 OE. Ion chromatography analysis measured six different cations: Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} and four different anions: Cl^- , NO_3^- , ClO_4^- , and SO_4^{2-} . Most ions were measured in all soil samples analyzed except for NH_4^+ at a depth of 30 cm and NO_3^- at a depth of zero centimeters. Additionally, the acid-base titration also measured HCO_3^- in the soils collected from the top 50 cm and CO_3^{2-} in the soils collected from ≥ 20 cm in depth. Due to the soils' overall high salinity, sample leachates were diluted 1,000-fold prior to analysis by IC. Therefore, it's possible that other ionic species were present in the soils in small concentrations, in the low mg/kg to $\mu\text{g}/\text{kg}$ range, which when diluted were below the detection limits of the instrument and therefore were not identified.

Figure 35 shows the soil profiles for the anions and cations in AT10 OE created by plotting the concentration of each ion in the soil (in mg/kg) as a function of soil depth (in cm). The dominant cation in AT10 OE was Na^+ and the dominant anion was SO_4^{2-} , suggesting a parent salt of $\text{Na}_2\text{SO}_4 \bullet 10\text{H}_2\text{O}$ (also known as mirabilite). Sodium sulfate is known to accumulate in the Atacama Desert from an oceanic origin of sea spray, marine aerosols and fog. [25, 73, 77, 97] However, the two ions do not show the same soil profile and there is significantly higher $[\text{SO}_4^{2-}]$ (in mM in the leachate solution) than $[\text{Na}^+]$ (in mM in the leachate solution) therefore other sulfate salts are also likely to be present throughout this pit. In fact, none of the cations appeared to be well correlated to a single anion, making for the determination of any potential parent salts difficult without further analysis.

AT10 6: Twelve soil samples were collected at 15 cm intervals in depth from AT10 6. Ion chromatography analysis measured four different cations:

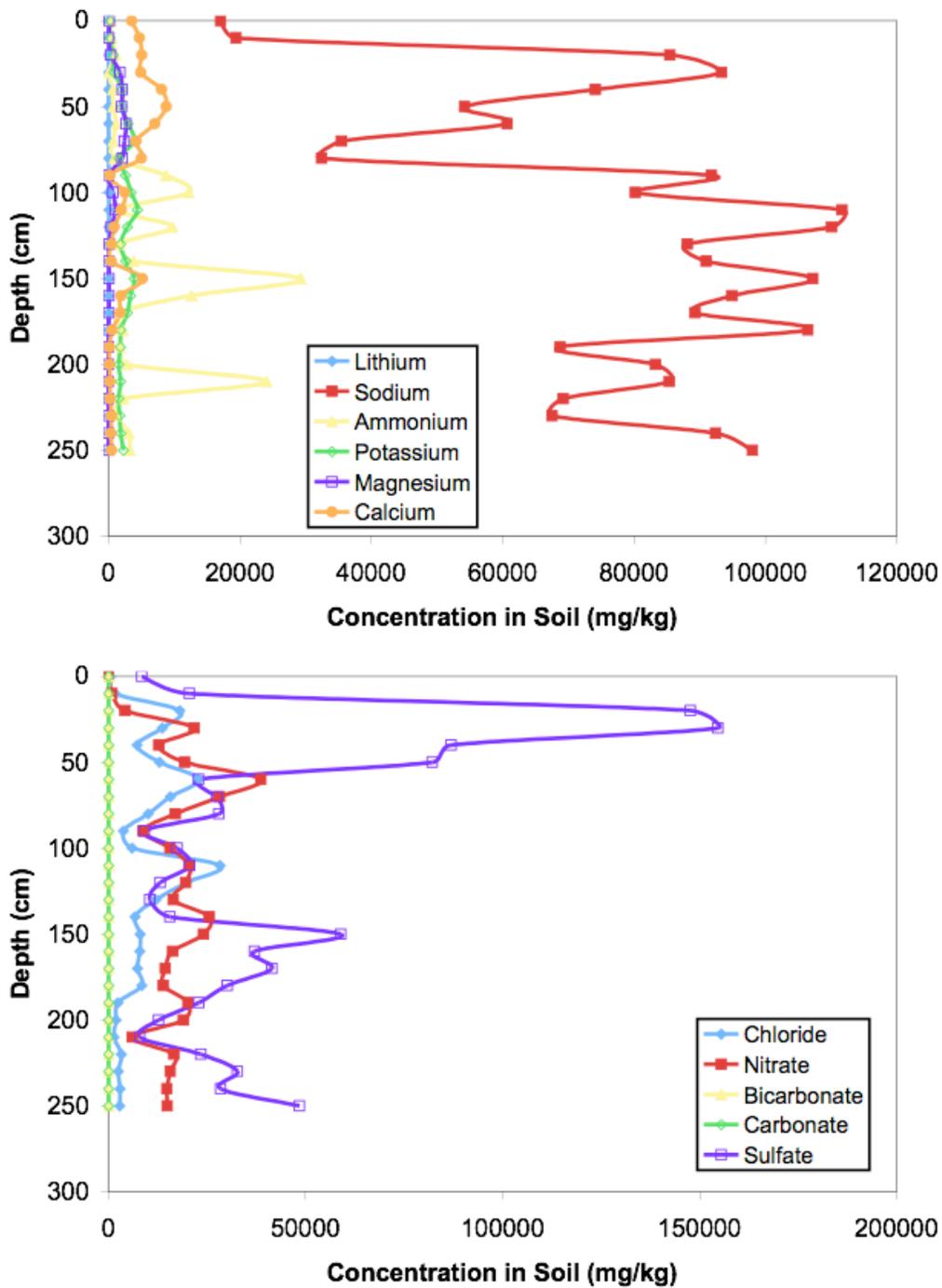


Figure 35: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when one gram of AT10 OE soil was leached in five milliliters of 18.2mΩ water for one hour and analyzed by IC and acid-base titration, as a function of depth (in cm)

Na^+ , K^+ , Mg^{2+} and Ca^{2+} and four different anions: Cl^- , NO_3^- , ClO_4^- , and SO_4^{2-} . The ions Na^+ , K^+ , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-} were measured in all soils analyzed. Perchlorate was measured at all but four depths, 0 cm, 15 cm, 30, and 155 cm, and Mg^{2+} was only present in measurable quantities in the soil above the caliche blanco at 170 cm in depth. Additionally, the acid-base titration also measured HCO_3^- in all soils and CO_3^{2-} in the soils collected 95 to 140 cm and 170 cm in depth. Due to the soils' overall high salinity, sample leachates were diluted 1,000-fold prior to analysis by IC. Therefore, it's possible that other ionic species were present in the soils in small concentrations, in the low mg/kg to $\mu\text{g}/\text{kg}$ range, which when diluted were below the detection limits of the instrument and therefore were not identified.

Figure 36 shows the soil profiles for the anions and cations in AT10 6 created by plotting the concentration of each ion in the soil (in mg/kg) as a function of soil depth (in cm). The dominant cation in AT10 6 was Na^+ and the dominant anion was SO_4^{2-} suggesting a parent salt of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (also known as mirabilite) which is known to accumulate in the Atacama Desert from an oceanic origin of sea spray, marine aerosols and fog. [25, 73, 77, 97] However, the two ions do not show the same soil profile indicating other Na^+ salts and sulfate salts are also likely to be present throughout the pit. The soil profiles of sodium and chloride are fairly well correlated, with much larger $[\text{Na}^+]$ than $[\text{Cl}^-]$, suggesting a likely parent salt of NaCl (also known as halite). Sodium chloride is known to accumulate in the Atacama Desert from an oceanic origin brought to the Desert by sea spray, marine aerosols and fog [25, 73, 77, 97] as well as from the weathering of continental evaporites [88, 97]. Aside from Na^+ and Cl^- , none of the other cations appear to be well correlated to a single anion making for the determination of any other potential parent salts difficult without further analysis.

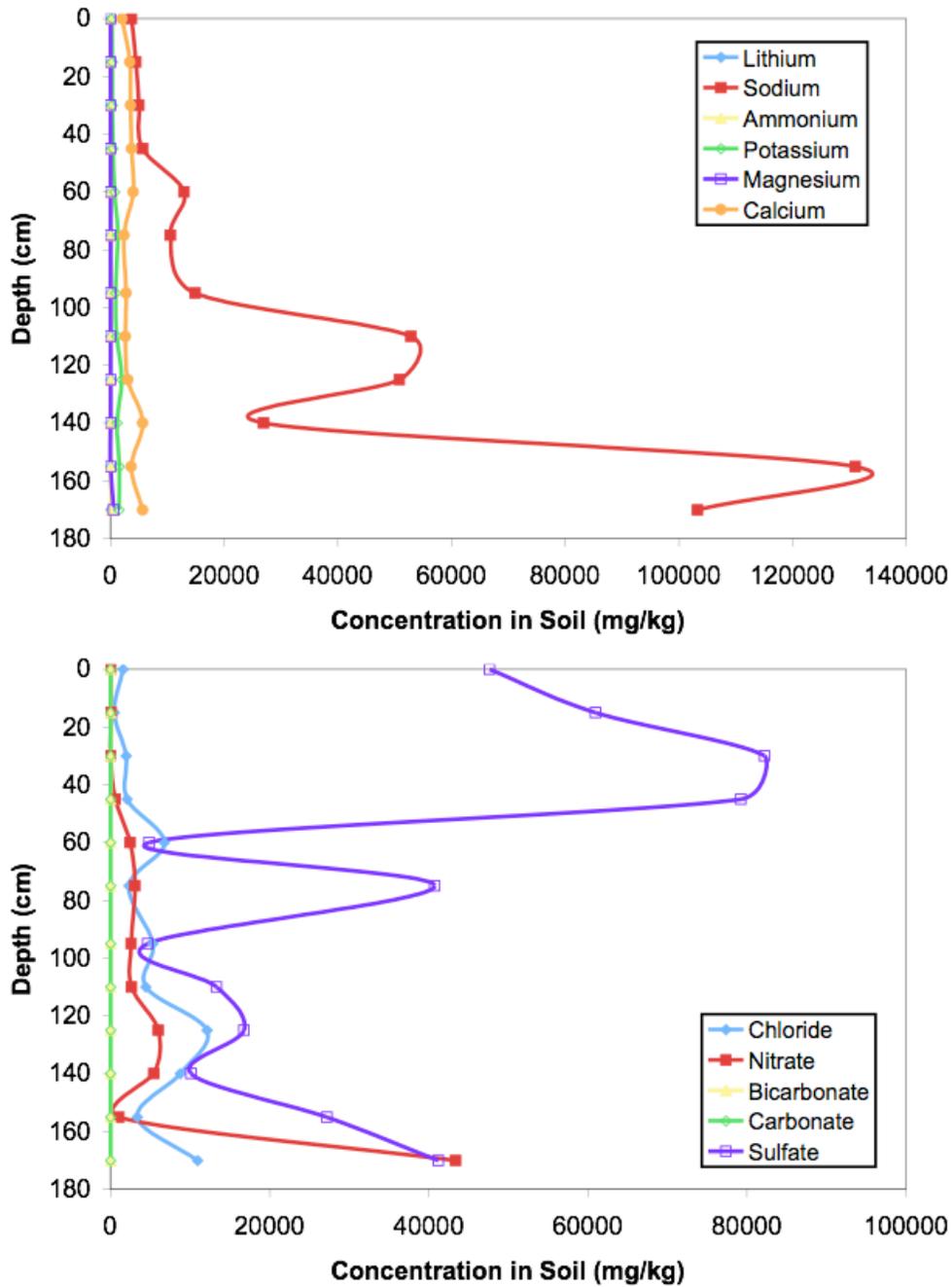


Figure 36: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when one gram of AT10 6 soil was leached in five milliliters of 18.2mΩ water for one hour and analyzed by IC and acid-base titration, as a function of depth (in cm)

Since the caliche blanco sample was close to 100% salt, it was not possible to analyze for cations and the majority of anions by IC. However, the sample was analyzed for perchlorate and it was present at levels of 21.72 μM in the caliche leachate solution (equivalent to 11 mg/kg in the original caliche sample). The nitrate test strips gave a ballpark concentration of 80.64 mM NO_3^- in the caliche leachate solution (equivalent to 1.25% NO_3^- in the original caliche sample), while the sulfate test strip recorded a ballpark concentration of >124 mM SO_4^{2-} in the caliche leachate solution (equivalent to >3% SO_4^{2-} in the original caliche sample). Finally, the EDX from the SEM-EDX analysis of several of the caliche sample salt crystals all showed peaks corresponding to sodium, sulfur and oxygen, identifying the crystals as sodium sulfate (also known as mirabilite). This finding helps to verify the finding of sodium sulfate in the other soils collected from this pit. The presence of high concentrations of nitrate and sulfate in at least the form Na_2SO_4 as well as some ClO_4^- in this caliche blanco sample is not unexpected as these species are common in caliche. [93, 94, 95, 96]

AT10 P: Eighteen soil samples of the top soil down to one centimeter in depth were collected over a linear transect of nine meters, AT10 P. Ion chromatography analysis measured six different cations: Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} and four different anions: Cl^- , NO_3^- , ClO_4^- , and SO_4^{2-} . All ions were present in all soil samples collected. Additionally, the acid-base titration also measured HCO_3^- in all soils. Due to the soils' overall high salinity, sample leachates were diluted 1,000-fold prior to analysis via IC. Therefore, it's possible that other ionic species were present in the soils in small concentrations, in the low mg/kg to $\mu\text{g}/\text{kg}$ range, which when diluted were below the detection limits of the instrument and therefore were not identified.

Figure 37 shows the soil transect for the anions and cations in AT10 P created by plotting the concentration of each ion in the soil (in mg/kg) as a function of linear distance from the first soil sample collected (in m). The dominant cations in this linear transect were Na^+ followed by Ca^{2+} and the dominant anions were Cl^- and SO_4^{2-} . The ions Na^+ and Cl^- follow the same trend along the entire linear transect. This suggests a parent salt of NaCl (also known as halite). Sodium chloride is known to accumulate in the Atacama Desert from an oceanic origin brought to the Desert via sea spray, marine aerosols and fog [97, 73, 25, 77] as well as from the weathering of continental evaporites [88, 97]. However, the $[\text{Na}^+]$ (in mM in the leachate solution) was much greater than $[\text{Cl}^-]$ (in mM in the leachate solution) at all points sampled along this transect. This suggests there were also additional sources contributing Na^+ to the soil. Additionally, Mg^{2+} and NO_3^- also follow the same trend across the linear transect as Na^+ and Cl^- but in much lower concentrations overall. Another pair of ions that follow the same trend along the entire linear transect are Ca^{2+} and SO_4^{2-} . This suggests a parent salt of CaSO_4 (also known as gypsum or anhydrite). Calcium sulfate, like NaCl , is also known to accumulate in the Atacama Desert. Sources of CaSO_4 include wind erosion [97] and direct volcanic emissions [88]. There is only slightly higher $[\text{Ca}^{2+}]$ (in mM in the soil leachate solution) than $[\text{SO}_4^{2-}]$ (in mM in the soil leachate solution) suggesting that CaSO_4 was the main source of these ions in this soil.

Decent (*i.e.*, $0.3 \leq R^2 \leq 0.5$) to good (*i.e.*, $R^2 \geq 0.5$) correlation was seen for Na^+ , K^+ , Mg^{2+} , and Ca^{2+} to the anions Cl^- , ClO_4^- , NO_3^- , and SO_4^{2-} . Therefore, any combination of these anion-cation pairs are possible parent salts in these soils. Further analysis is necessary to determine these pairings.

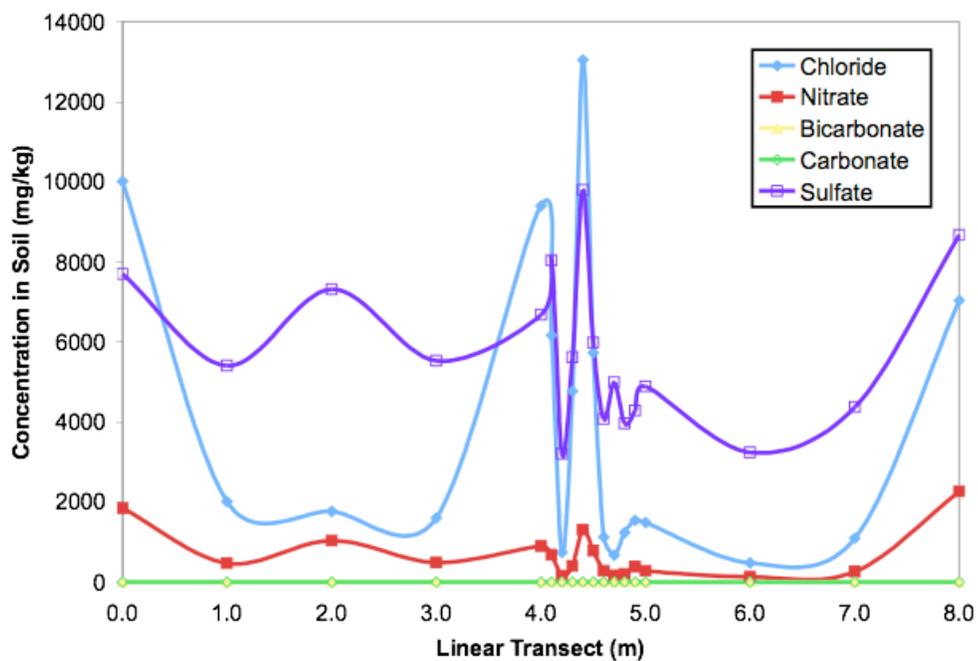
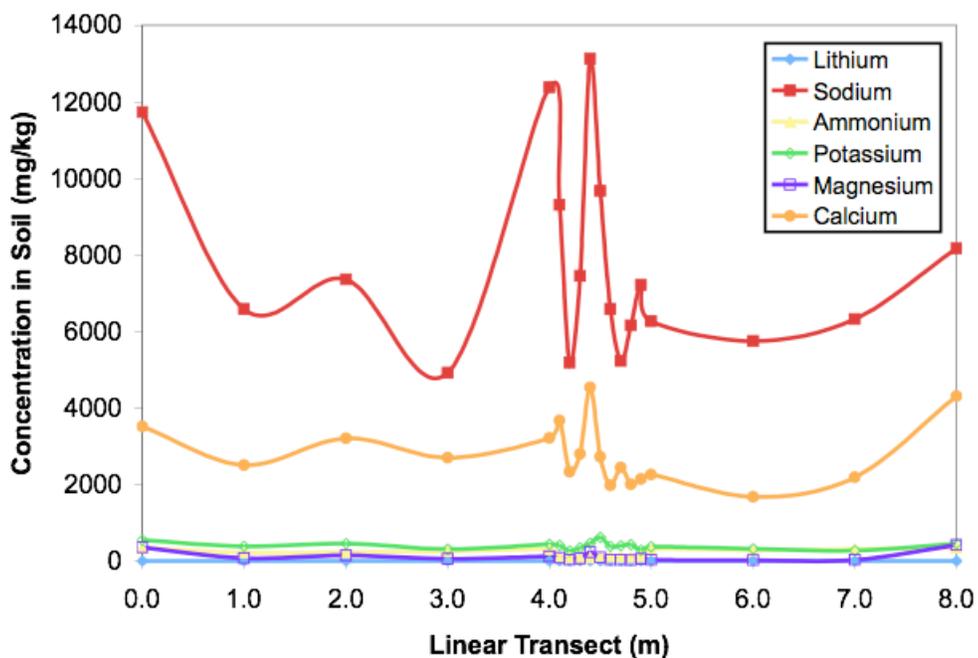


Figure 37: Plot of the concentration (in mg/kg) of cations (on top) and anions (on bottom) in the soil, when one gram of AT10 P soil was leached in five milliliters of 18.2mΩ water for one hour and analyzed by IC and acid-base titration, as a function of distance (in m)

Wet Chemistry Laboratory Results: The WCL is only capable of detecting and quantifying nine ions, Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , and NO_3^- or ClO_4^- . It is known from the IC analysis that the ratio of $\text{NO}_3^-:\text{ClO}_4^-$ in soils where ClO_4^- was detected was large, ranging from $\sim 640\text{-}9000:1$. Due to the large $\text{NO}_3^-:\text{ClO}_4^-$ in the MDV soils studied by IC and selectivity of the $\text{NO}_3^-:\text{ClO}_4^-$ electrode, this electrode was considered to be a NO_3^- ISE for these samples. As with the MDV analysis, only a subset of the Atacama soil samples was analyzed by WCL. Five soil samples spread throughout the pit or transect were analyzed from each of the three locations: depths of 0 cm, 15 cm, 75 cm, 125 cm and 170 cm in AT10 6, depths of 0 cm, 30 cm, 120 cm, 180 cm and 240 cm in AT10 OE and distances of 0 m, 3 m, 4.4 m, 4.7 m and 8 m along AT10 P.

The WCL data analysis of some soils from the Atacama was not as straight forward as the analysis of the MDV soils due to the presence of measurable quantities of Li^+ (>0.01 mM in the soil leachate solution or >1 mg/kg in the soil) in all soils at locations AT10 OE and AT10 P as measured by IC. Since the WCL uses the Li^+ ISE as a reference it required the concentration of Li^+ remain constant throughout the experiment, within the standard deviation given by the ~ 4 mV of noise from the Li^+ ISE. Therefore, any samples containing more than ~ 0.2 mM of Li^+ required the excess Li^+ concentration be subtracted from the data prior to determining the mV change for each of the other ISEs. Using the concentration of Li^+ determined by the IC, the corresponding change in mV response was calculated. This mV value was subtracted from the mV response of each of the other ISEs upon sample addition. Then the concentration of each ion was then calculated from the corrected mV response.

Of the nine ions detectable by WCL, six (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}

and Ba^{2+}) were detected at measurable quantities in all soil analyzed in all three location. Measurable Cl^- and NO_3^- was not found in the 0 cm or 15 cm depth samples in AT10 6 or the 0 cm depth sample in AT10 OE. One sample analyzed along the AT10 P, 4.7 m, also did not have a measurable quantity of NO_3^- . Tables listing the concentration of each soluble ion in each soil sample detected and quantified by WCL can be found in Appendix H.

In compiling the data from the WCL analysis, there were some similarities and differences in the WCL data as compared to the IC data of the corresponding samples. The same kinds of discrepancies were also found when analyzing the McMurdo Dry Valleys (see Chapter 2) such as the IC data detecting concentrations of Na^+ which were one to three order of magnitude higher than the concentrations of Na^+ detected by WCL. In Chapter 2, rationale was given to justify the discrepancies seen between the WCL and IC data in the MDV soils. The same justifications can be used for these samples as well. These are natural and complex samples, and while sieved to remove large particles are subject to heterogeneity between soil samples. Additionally, the same issues with the WCL testbed and its lack of Li^+ selectivity potential also affected the results of this analysis. Therefore, due to the limitations encountered in running the WCL for the determination of soluble ions only the IC data for soluble ions will be discussed when comparing the soils from the locations in the Atacama Desert and the subsequent comparison of the Atacma soils to the soil on Mars at the Phoenix Lander site and these samples were also not used in cataloging for the Phoenix mission.

4.4.2 Comparison of the Ions in All Three Locations

Overall, there were some similarities as well as some differences in the soluble ions present in the soils from the two pits and one linear transect collected

from varying locations in the Atacama Desert. The most noticeable difference is in the number of different ions found in measurable quantities at the three locations. All three locations exhibited high levels of Na^+ , Ca^{2+} , Cl^- and SO_4^{2-} with measurable quantities of K^+ , Mg^{2+} , NO_3^- , ClO_4^- , and HCO_3^- . However, there was no measurable Li^+ or NH_4^+ in any of the soils collected from AT10 6 and there was no CO_3^{2-} in any of the soils at AT10 P. The lack of CO_3^{2-} was not unexpected, because all the soils from this linear transect were collected at a depth of ~ 1 cm and there was no measurable CO_3^{2-} in the soils collected from this depth at AT10 OE or AT10 6. However, the lack of measurable Li^+ or NH_4^+ in AT10 6 was unexpected. Both Li^+ and NH_4^+ accumulate in soils due to volcanic emissions. [88, 97] Since volcanos are scattered along the Andes mountains, it was interesting to find no measurable quantities of these ions in the pit dug at the location of AT10 6.

Perchlorate: Perchlorate was detected in the soils from all three of the locations, AT10 6, AT10 OE and AT10 P. Tables 30, 31 and 32 lists the concentration of perchlorate in each of the soil samples from AT10 6, AT10 OE and AT10 P, respectively. There was only four soils, all from AT10 6 that did not have measurable quantities of ClO_4^- , meaning the concentration of ClO_4^- in these soils were $<0.05 \mu\text{M}$ in the soil leachate solution or $<25 \mu\text{m}/\text{kg}$ in the soil. The concentration of ClO_4^- in these soils ranged from $M < 0.05$ to $15.51 \mu\text{M}$ in the soil leachate solution (or <25 to $7713 \mu\text{g}/\text{kg}$ in the soil) at AT10 6, from 0.36 to $122.03 \mu\text{M}$ in the soil leachate solution (or 181 to $60668 \mu\text{g}/\text{kg}$ in the soil) at AT10 OE and 0.14 to $5.41 \mu\text{M}$ in the soil leachate solution (or 71 to $2687 \mu\text{g}/\text{kg}$ in the soil) at AT10 P. Therefore, it appears that ClO_4^- is ubiquitous across the Atacama Desert.

Figure 38 shows the $[\text{ClO}_4^-]$ (in mg/kg) versus depth (in cm) for the two

Table 30: List of the soil samples from the Atacama Desert at location AT10 6 and their corresponding concentrations of perchlorate in both the soil leachate solution (in μM) and the original soil samples (in $\mu\text{g}/\text{kg}$) when one gram of soil is leached in 5 mL of 18.2 m Ω water for one hour and analyzed by IC. The standard deviation was $<\pm 30\%$ for all measurements.

| Soil | Concentration in Solution | Concentration in Soil |
|----------------|---------------------------|-----------------------------|
| Identification | (μM) | ($\mu\text{g}/\text{kg}$) |
| AT10 6 0cm | < 0.05 | < 25 |
| AT10 6 15cm | < 0.05 | < 25 |
| AT10 6 30cm | < 0.05 | < 25 |
| AT10 6 45cm | 0.46 | 229 |
| AT10 6 60cm | 2.75 | 1368 |
| AT10 6 75cm | 6.44 | 3197 |
| AT10 6 95cm | 10.47 | 5199 |
| AT10 6 110cm | 8.39 | 4166 |
| AT10 6 125cm | 11.99 | 5958 |
| AT10 6 140cm | 12.87 | 6398 |
| AT10 6 155cm | < 0.05 | < 25 |
| AT10 6 170cm | 15.51 | 7713 |

pits, AT10 6 and AT10 OE, and the $[\text{ClO}_4^-]$ (in mg/kg) versus linear transect (in m) for AT10 P. The amount of perchlorate at locations AT10 6 and AT10 P accounts for 0.01% of the total ion content, while at AT10 OE the amount of perchlorate accounts for 0.03% of the total ion content. These values are slightly lower than the 0.03 to 0.6 wt.% perchlorate previously reported in the Atacama. [44] In all three locations, the trend of perchlorate down the pits and across the linear transect matches closely to the trends of nitrate and chloride but the perchlorate is present in much smaller quantities. The similarity in profiles suggests a possible correlation between ClO_4^- and NO_3^- and ClO_4^- and Cl^- .

Figure 39 plots the concentration of perchlorate in the soil (in mg/kg) versus the concentration of Cl^- and NO_3^- in all three of the Atacama locations, AT10 6, AT10 OE and AT10 P. Some correlations were seen between anions in these soils; when plotting the concentration in mg/kg in the soil of perchlorate

Table 31: List of the soil samples from the Atacama Desert at location AT10 OE and their corresponding concentrations of perchlorate in both the soil leachate solution (in μM) and the original soil samples (in $\mu\text{g}/\text{kg}$) when one gram of soil is leached in 5 mL of 18.2 m Ω water for one hour and analyzed by IC. The standard deviation was $<\pm 25\%$ for all measurements.

| Soil Identification | Concentration in Solution (μM) | Concentration in Soil ($\mu\text{g}/\text{kg}$) |
|---------------------|---|---|
| AT10 OE 0cm | 0.36 | 181 |
| AT10 OE 10cm | 2.56 | 1270 |
| AT10 OE 20cm | 2.15 | 1069 |
| AT10 OE 30cm | 22.24 | 11049 |
| AT10 OE 40cm | 47.20 | 23432 |
| AT10 OE 50cm | 62.19 | 30916 |
| AT10 OE 60cm | 60.21 | 29941 |
| AT10 OE 70cm | 75.67 | 37655 |
| AT10 OE 80cm | 51.73 | 25703 |
| AT10 OE 90cm | 22.41 | 11143 |
| AT10 OE 100cm | 24.53 | 12192 |
| AT10 OE 110cm | 87.83 | 43659 |
| AT10 OE 120cm | 68.23 | 33906 |
| AT10 OE 130cm | 45.60 | 22679 |
| AT10 OE 140cm | 97.67 | 48554 |
| AT10 OE 150cm | 122.03 | 60668 |
| AT10 OE 160cm | 59.34 | 29516 |
| AT10 OE 170cm | 65.74 | 32676 |
| AT10 OE 180cm | 40.68 | 20199 |
| AT10 OE 190cm | 46.76 | 23254 |
| AT10 OE 200cm | 21.52 | 10692 |
| AT10 OE 210cm | 26.42 | 13133 |
| AT10 OE 220cm | 18.78 | 9344 |
| AT10 OE 230cm | 14.39 | 7142 |
| AT10 OE 240cm | 11.55 | 5742 |
| AT10 OE 250cm | 13.70 | 6800 |

Table 32: List of the soil samples from the Atacama Desert at location AT10 P and their corresponding concentrations of perchlorate in both the soil leachate solution (in μM) and the original soil samples (in $\mu\text{g}/\text{kg}$) when one gram of soil is leached in 5 mL of 18.2 m Ω water for one hour and analyzed by IC. The standard deviation was $<\pm 20\%$ for all measurements.

| Soil | Concentration in Solution | Concentration in Soil |
|----------------|---------------------------|-----------------------------|
| Identification | (μM) | ($\mu\text{g}/\text{kg}$) |
| AT10 P 21 | 5.41 | 2687 |
| AT10 P 22 | 0.79 | 392 |
| AT10 P 23 | 1.31 | 649 |
| AT10 P 24 | 0.67 | 335 |
| AT10 P 25.0 | 1.64 | 814 |
| AT10 P 25.1 | 0.77 | 284 |
| AT10 P 25.2 | 0.21 | 104 |
| AT10 P 25.3 | 0.77 | 385 |
| AT10 P 25.4 | 2.62 | 1305 |
| AT10 P 25.5 | 1.44 | 716 |
| AT10 P 25.6 | 0.34 | 170 |
| AT10 P 25.7 | 0.17 | 86 |
| AT10 P 25.8 | 0.19 | 95 |
| AT10 P 25.9 | 0.61 | 302 |
| AT10 P 26 | 0.37 | 182 |
| AT10 P 27 | 0.14 | 71 |
| AT10 P 28 | 0.27 | 133 |
| AT10 P 29 | 4.94 | 2455 |

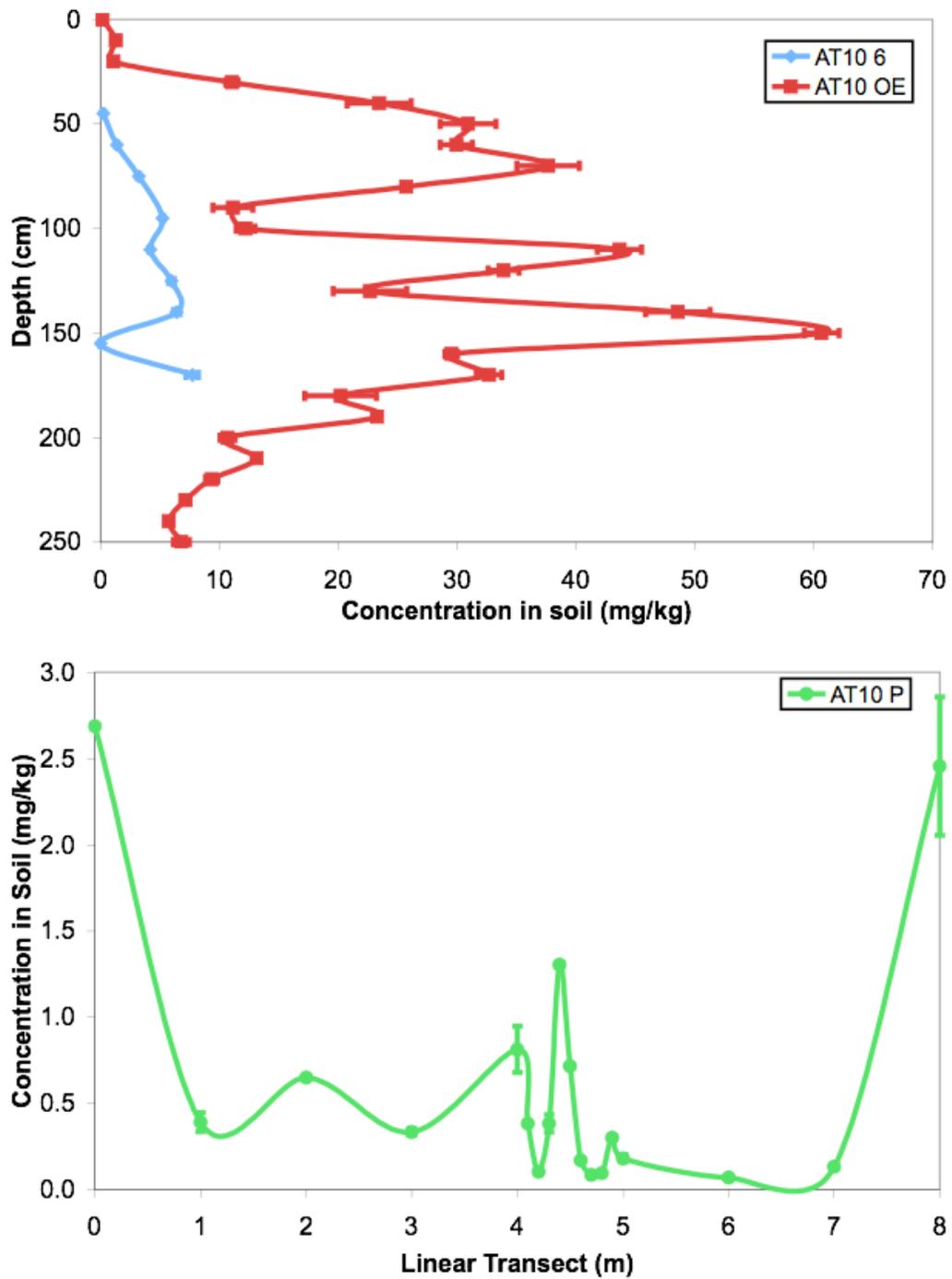


Figure 38: Plot of the concentration (in mg/kg) perchlorate in the soils, when one gram of soil was leached in five milliliters of 18.2mΩ water for one hour and analyzed by IC, as a function of depth (in cm) for AT10 6 and AT10 OE (top) and as a function of distance (in m) for AT10 P.

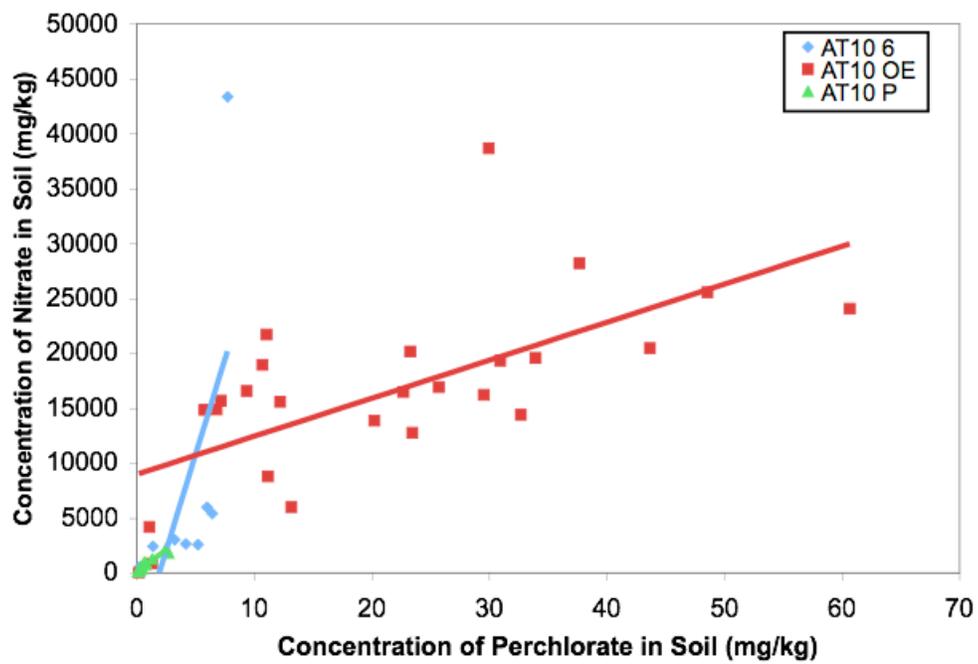
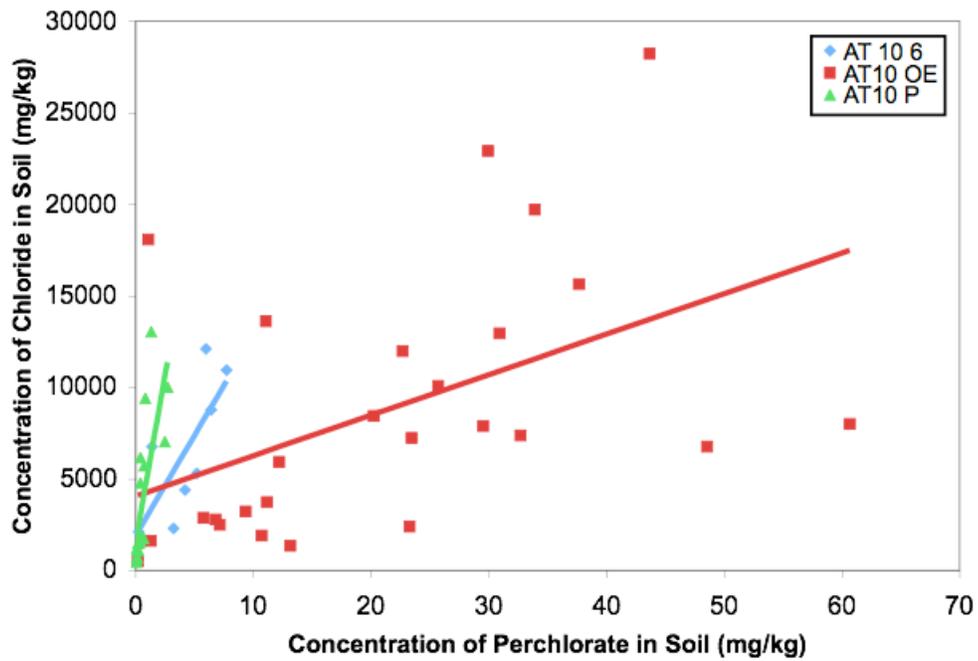


Figure 39: Correlation of perchlorate to other anions in the Atacama: chloride (top) and nitrate (bottom)

versus another anion. Decent (*i.e.*, $0.3 \leq R^2 \leq 0.5$) to good (*i.e.*, $R^2 \geq 0.5$) correlations were seen for ClO_4^- to NO_3^- in all three locations ($R^2 = 0.3886$, 0.4280 and 0.5407 for AT10 6, AT10 OE and AT10 P, respectively). Good correlation was also seen for ClO_4^- to Cl^- in AT10 6 and AT10 P ($R^2 = 0.5535$ and 0.5407 , respectively), but was not as strong from AT10 OE ($R^2 = 0.2255$). As for ClO_4^- to SO_4^{2-} good correlation was seen for AT10 P ($R^2 = 0.5318$) but there was no correlation for AT10 6 or AT10 OE. This suggests Cl^- , NO_3^- , and ClO_4^- share a somewhat common depositional source, most likely atmospheric because these three anions are thought to form in the stratosphere [25, 73, 77] but there are other depositional inputs that add to the overall concentrations of each anion, especially Cl^- at AT10 OE. The lack of correlation of ClO_4^- to SO_4^{2-} at AT10 6 and AT10 OE suggests the majority of SO_4^{2-} in these pits is from other sources, such as a marine input, wind erosion, volcanic rocks, and volcanic emissions. [25, 73, 77, 97]

Relative Abundance of Ions: Figure 40 shows the relative abundance of each anion and cation calculated from the total concentration of each ion (mg/kg in the soil) within the two pits: AT10 OE and AT10 6. The most abundant cation in each pit was Na^+ . This cation accounts for $\sim 88\%$ of the total cations quantified in both pits. Both pits also had approximately the same abundance of K^+ ($\sim 2.5\%$). The second most abundant ion in AT10 OE was NH_4^+ at $\sim 5.6\%$ was not measurable in AT10 6, followed by Ca^{2+} at $\sim 3\%$. In AT10 6, Ca^{2+} was the second most abundant cation at 8.9% , which was roughly the same abundance of NH_4^+ and by Ca^{2+} combined in AT10 OE. The abundance of Mg^{2+} and Li^+ in both pits was very small, together accounting for $>1\%$ of the total cations.

The anions in both pits were dominated by Cl^- , NO_3^- , and SO_4^{2-} , with

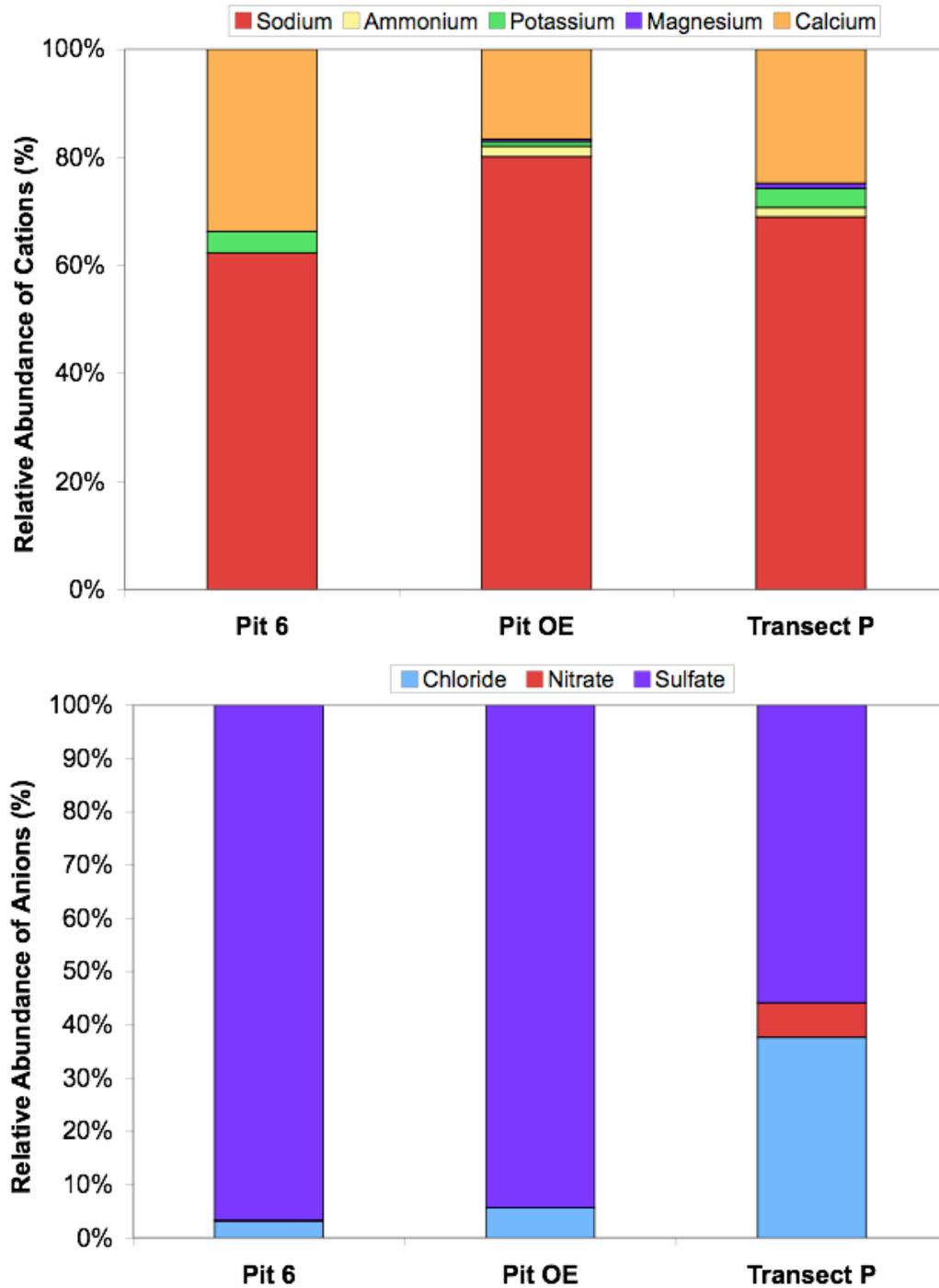


Figure 40: Relative abundance of cations (on top) and anions (on bottom) in the soils from the Atacama Desert at locations AT10 6 and AT10 OE

ClO_4^- , HCO_3^- , and CO_3^{2-} accounting for only a fraction of a percent in both pits. The most abundant anion in both pits was SO_4^{2-} , accounting for $\sim 61\%$ and $\sim 77\%$ of all anions quantified in AT10 OE and AT10 6, respectively. Nitrate was the next most abundant in both pits, $\sim 25\%$ in AT10 OE and $\sim 12\%$ in AT10 6, followed by Cl^- , with $\sim 14\%$ and $\sim 11\%$ in AT10 OE and AT10 6, respectively.

The linear transect soils were collected at a depth of ~ 1 cm. Figure 41 shows the relative abundance of each anion and cation calculated from the total concentration of each ion (mg/kg in the soil) across the linear transect AT10 P was compared to the abundance of each anion and cation calculated from the concentration of each ion (mg/kg in the soil) in the topsoil (0 cm soil sample) collected in each of the two pits, AT10 OE and AT10 6. Overall, the most abundant cation in all three locations was Na^+ with $>80\%$ total cation abundance followed by Ca^{2+} with $>16\%$ total cation abundance. The top soil from AT10 6 and the AT10 P possessed a similar abundance of K^+ (3.5-4% of the total cations) while the top soil from AT10 OE had a little less than 1% of the total cations. The top soil from AT10 6 did not have any measurable amount of either NH_4^+ or Mg^{2+} , while the top-soil of AT10 OE and AT10 P possessed a similar abundance of both (1.8-2% NH_4^+ and 0.4-0.9% Mg^{2+}). The abundance of Li^+ was very small or non-measurable at all three locations accounting for only a fraction of a percent of the total cations.

The most abundant anion in all three locations was SO_4^{2-} at $> 55\%$ total anion abundance. However, there was significantly more SO_4^{2-} in the top soils from AT10 6 and AT10 OE ($\sim 97\%$ and $\sim 94\%$, respectively) than in the soils from AT10 P ($\sim 56\%$ abundance). The soils from the linear transect had a higher abundance of Cl^- ($\sim 38\%$) compared to the two pits ($\sim 3\%$ and $\sim 6\%$ total anion abundance in AT10 6 and AT10 OE, respectively). Likewise, there

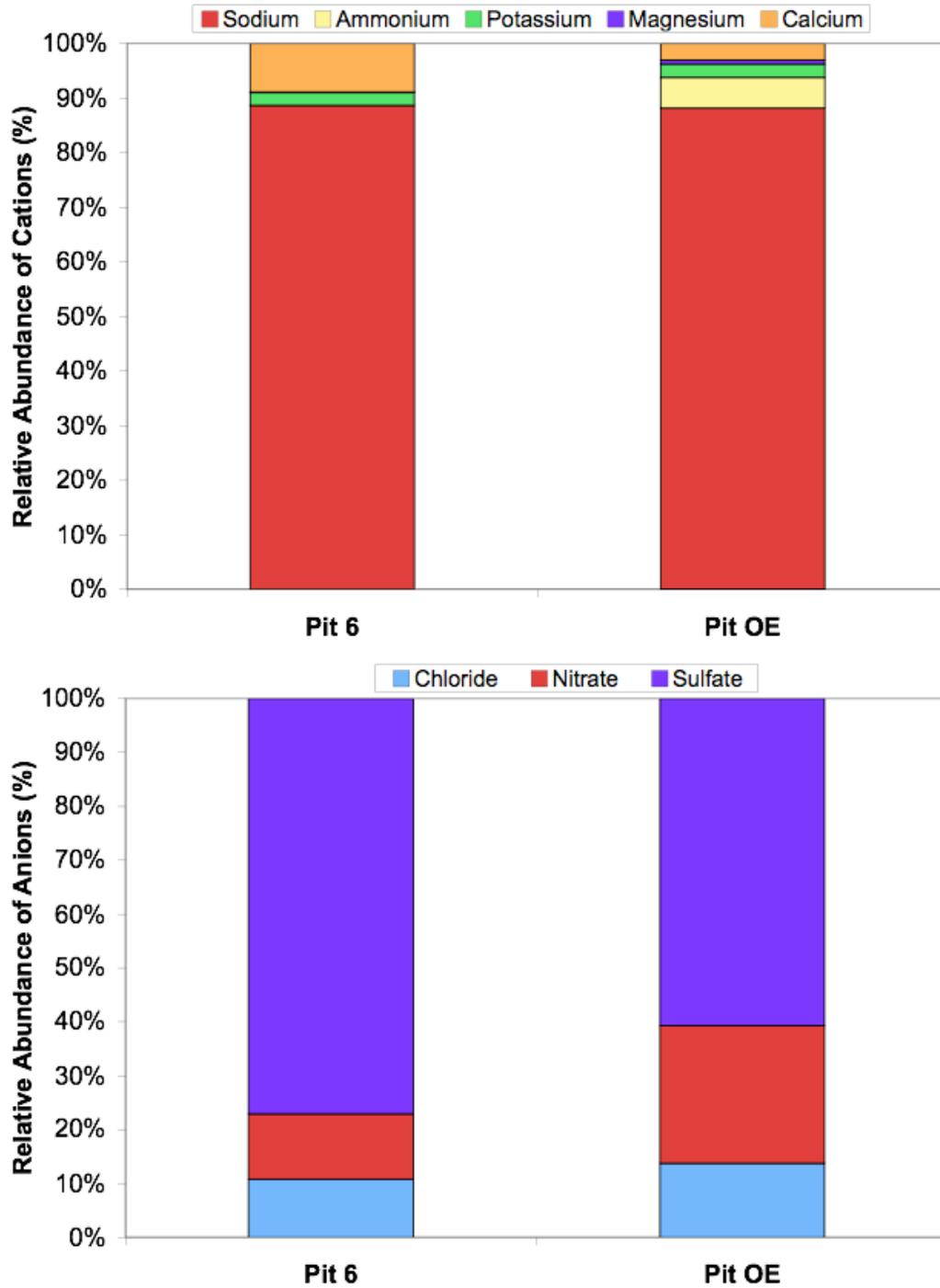


Figure 41: Relative abundance of cations (on top) and anions (on bottom) in Atacama Desert top 5 cm of soil from all three locations: AT10 6 , AT10 OE and AT10 P

was a noticeable contribution of NO_3^- to the linear transect soils ($\sim 6\%$), but $>1\%$ abundance of NO_3^- in the top soil from AT10 6 and AT10 OE. The abundance of ClO_4^- , HCO_3^- and CO_3^{2-} was very small at all three location together accounting for only a fraction of a percent of the total anions.

No matter the location of sampling, the soils collected from the Atacama were found to be dominated by Na^+ and SO_4^{2-} with substantial concentrations of Ca^{2+} , Cl^- , and NO_3^- and smaller concentrations of K^+ and ClO_4^- . Measurable concentrations of Li^+ , NH_4^+ , CO_3^{2-} and Mg^{2+} were present in two of the three locations (though Mg^{2+} was measured at a depth of 170 cm at AT10 6).

The soil profiles down the pits varied considerably between the two pits (see Figures 35 and 36) and the concentration of ions (in mg/kg in the soil) varied by up to an order of magnitude for some ions within the soil profiles, down the pit or across the linear transect.

Sampling Resolution: The soil profiles for AT10 OE and AT10 6 varied considerably between the two pits (Figures 35 and 36). Likewise, neither of the soil profiles matched the shape of any of the soil profiles in the MDV. The majority of the pits in the MDV, Pits 1 (Figure 13), 3 (Figure 16), 4 (Figure 15), 9 (Figure 18), 11 (Figure 20), 13 (Figure 19), and 20 (Figure 21), have the highest concentration of most ions just below the top soil and the ion concentrations decreased with depth. In the Atacama, the pit profiles are much more complex. This is due in part to the resolution of pit sampling. Many more samples were collected in the Atacama pits to a much deeper depth. Additionally, the sampling was performed at regular intervals due to the lack of soil horizons with distinct salt layers seen the MDV. In most instances, the number of soil samples collected from the pits in the MDV were limited by

the number of soil horizons to the permafrost layer but a permafrost layer was not reached in Pit 11 in Beacon Valley dug to a depth of 105 cm. Only three samples were collected from 7 to 105 cm at 25 cm intervals. If there was greater resolution in pit sampling, the results from the two pits dug in the Atacama suggest this profile would appear much more complex.

In addition to the sampling resolution affecting the overall shape/complexity of the pit profiles, it also affects the ability to discern the soil's uniformity (*i.e.*, the homogeneity or heterogeneity of the soil) either down a pit or across a linear transect. In the Atacama soil samples from all three locations the concentrations of some ions (in ppm in the soil) varied by up to an order of magnitude within the soil profiles. At location AT10 P, there was an order of magnitude difference in the concentration of Mg^{2+} , Cl^- , NO_3^- , and ClO_4^- (in ppm in the soil) along the 8 meter long linear transect of the top soil. The result highlights the heterogeneity of the soil within a very small sampling area. This has implications for the findings of WCL aboard the Phoenix mars Lander. Three soil samples were collected and analyzed from a small area of the robotic arm's reach. The two samples of comparable size of 1 cm^3 , Rosy Red and Sorceress 2, were collected from trenches dug close together and contained similar concentrations of all ions (with error in concentrations of $\pm 20\%$ for +1 and -1 ions and $\pm 50\%$ for +2 ions). If the samples were collected from locations that were further apart (yet even as close as 1 m) the Atacama results for AT10 P show the ionic content of the soils could have been much more varied.

4.4.3 Analysis of the Unknown Precipitate

Soil samples were prepared for analysis according to the procedure outline for IC analysis and the filtered leachate solution was stored in glass vials on the benchtop at room temperature. Within 24 hours, small needle-like salt

crystals formed at the bottom of several of the vials. Visible amounts of this precipitate were present in seven of the 25 samples collected from AT10 OE at depths of 20 cm, 30 cm, 40 cm, 50 cm, 80 cm, 150 cm, and 160 cm, as well as six of the 12 samples collected from AT10 6 at depths of 45 cm, 110 cm, 125 cm, 140 cm, 155 cm and 170 cm (the sample of caliche blanco was not tested). No precipitate formed in any of the soils from AT10 P.

The salt crystals were analyzed by SEM-EDX. Figure 42 shows the EDX spectra for one of the salt crystals analyzed. The EDX shows peaks corre-

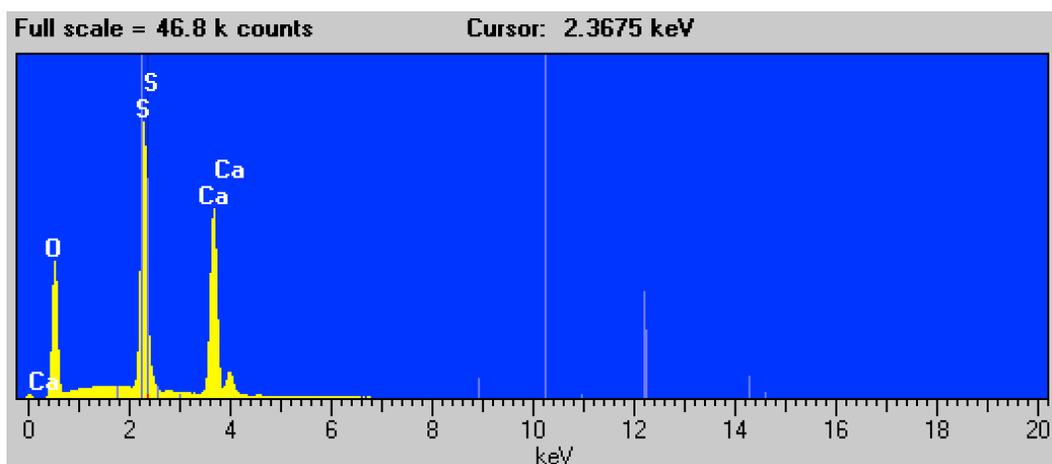


Figure 42: EDX spectra of a precipitate salt crystal formed in the soil leachate solution a soil sample from the Atacama Desert

sponding to calcium, sulfur and oxygen, identifying the crystal as calcium sulfate. Several different salt crystals were tested from several samples from both pits and the composition was consistently calcium sulfate in all samples. However, in some crystals there were also peaks for sodium and chloride. It is believed that sodium chloride is a contaminant present because of the way in which the crystals were dried prior to analysis. The crystals were not washed and therefore it is assumed some sodium and chloride from solution remained behind on the outside of the crystals when the solution was poured out and dried as sodium chloride.

Though the salt crystals were positively identified as CaSO_4 , this does not automatically indicate the presence of the parent salt gypsum (CaSO_4) or anhydrite ($\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$) in the soil. While it is likely that one or more forms of CaSO_4 is present in the soil, the precipitate is more likely the result of Ca^{2+} from one parent salt combining in solution with SO_4^{2-} from a separate parent salt and forming the resulting precipitate due to the high concentrations of SO_4^{2-} in these soils and the sparingly soluble nature of CaSO_4 ($k_{sp} = 4.93\text{E-}5$ 25°C [99]) compared to the other sulfate salts.

4.4.4 pH, Conductivity and Ionic Strength

In addition to analyzing the soils from the Atacama to determine their soluble ion content, the soil solution pH and solution electrical conductivity were measured and the ionic strength was calculated. Analysis of these other soil properties is important to allow for a better overall understanding of the soil from this environment. The results from each analysis is discussed and a comparison is made between the Atacama soils and soil from the northern polar region of Mars.

pH: The pH of all soil samples leached one hour with a 1:5 (wt:vol) soil-to-water ratio using 1 gram of soil and 5 mL of 18.2 m Ω water was measured with a commercial pH probe. The pH probe was calibrated each day prior to analysis with commercial premixed buffer solutions of pH 4, 7 and 10. The slope of the pH calibration varied from 98.8 to 99.9 over the course of this analysis.

AT10 6 and AT OE: Figure 43 depicts the pH profile for the two vertical pits, AT10 6 and AT10 OE. Soils from the two vertical pits vary in pH from slightly acidic to slightly basic with a low of 6.21, at the surface soil horizon

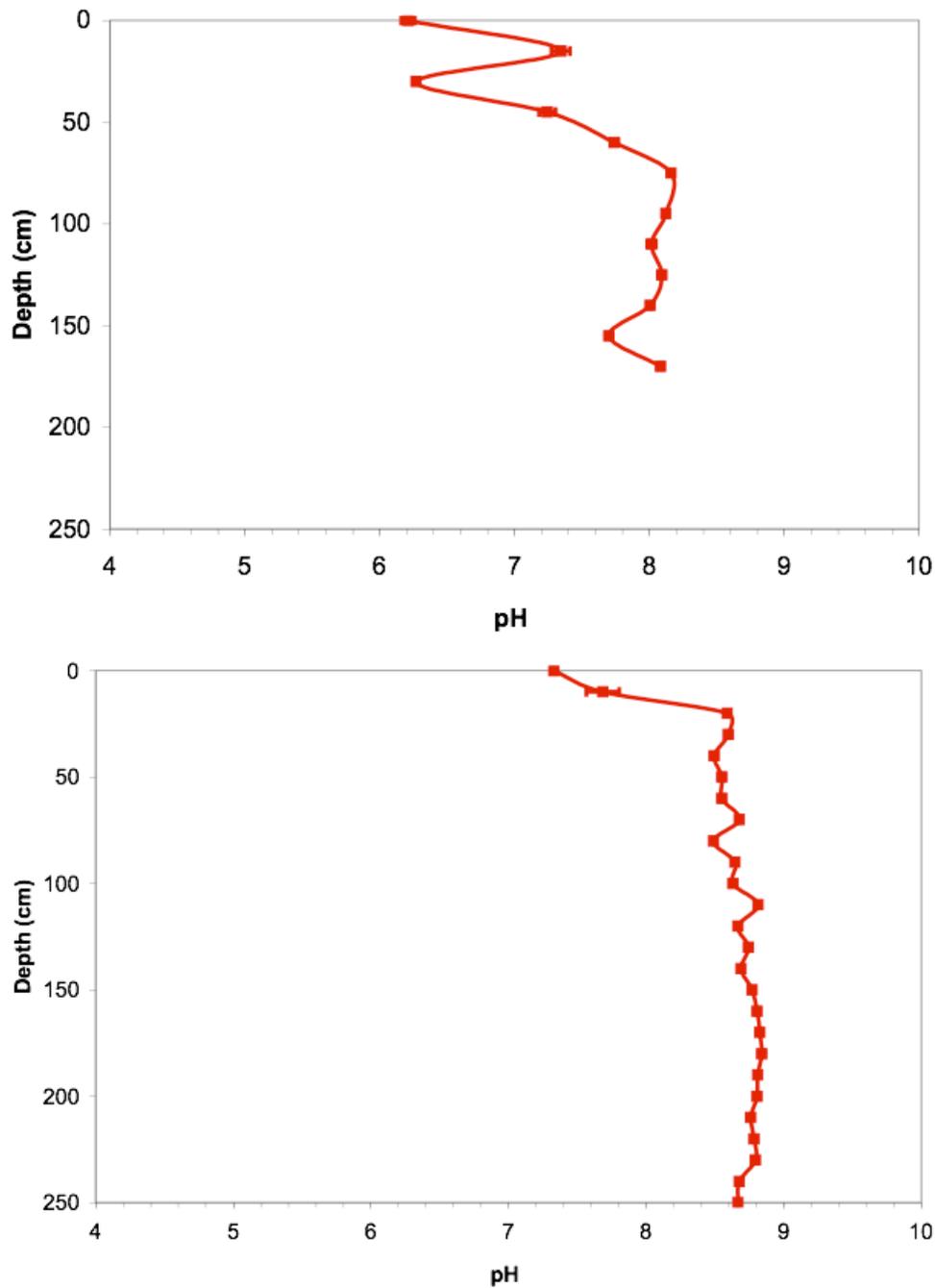


Figure 43: pH profiles of Atacama Desert soil leachates from Pit AT10 6 (on top) and Pit AT10 OE (on bottom) . One gram of each soil was leached in five milliliters of 18.2 mΩ water for one hour then filtered before the pH was measured with a commercially available pH probe.

of AT10 6, to a high of 8.84, at a depth of 180cm in AT10 OE. Overall, the soil pH was more basic in AT10 OE, ranging from 7.33 to 8.84, than in AT10 6, which ranged from 6.21 to 8.16. In both vertical pits, the slightly acidic pH was found near the pit's surface. All soils below 60 cm were found to be of pH 8 or greater with one exception.

The pH range for soils from both pits is comparable to the pH range of soils collected from two previous studies of Atacama soils, both collected in the area close to the location of AT10 6. In a study by Bagaley [100], the equilibrated pH of 33 soil samples from 4 different pits was reported to range from 7.16 to 8.27, while Quinn et al. [28] reported an equilibrated pH range from 6.8 to 8.5 for 12 soil samples collected from a single pit. A slightly acidic pH of 6.8 in the surface level soil sample seen by Quinn et al [28] is consistent with the slightly acidic pH of 6.2 seen in AT10 6.

In the work by Quinn et al. [28], the pH was monitored from the time the soil was first introduced to the water until the measurements approached equilibrium. By using this method it was possible to track any changes in the pH with time. This test revealed a rapid shift to an acidic pH (as low as pH 4.3) when the soil was first introduced to the water followed by an equilibration to a more basic pH in soil from the surface but not in the soils from the subsurface. Quinn et al. attributed this pH response to a soluble acid present in the soil, which is neutralized rapidly by other soil components when the soluble species are dissolved in water. [28]

To test for a similar phenomenon in the soils collected for this work, samples from the surface of both pits, AT10 6 0 cm and AT10 OE 0 cm, as well as a soil from the subsurface of both pit AT10 6 140 cm and AT10 OE 200 cm, were re-analyzed for pH, monitoring the pH for one hour (the length of time the soils were leached before being filtered and analyzed for pH in the original

study) starting at the time of soil addition. All four soil samples showed a similar rapid shift to acidic pH (ranging from pH 4 to 5.3) when the soil was first added followed by equilibration to a more neutral to basic pH. All soils had reached pH equilibrium by the end of the one hour test. From the analysis of soluble species present in these soils, it is likely the theory by Quinn et al. [28] of the neutralization of a soluble acid by other soil components is correct, because the acid-base titrations of these soils revealed the presence of species capable of neutralizing an acidic salt: HCO_3^- in samples AT10 6 0 cm and AT10 OE 0cm, CO_3^{2-} in sample AT10 OE 200 cm, and both HCO_3^- and CO_3^{2-} in sample AT10 6 140 cm.

AT10 P: Figure 44 depicts the pH profile for the horizontal soil profile. Soils from the linear transect are all very neutral in pH ranging from pH 7.42

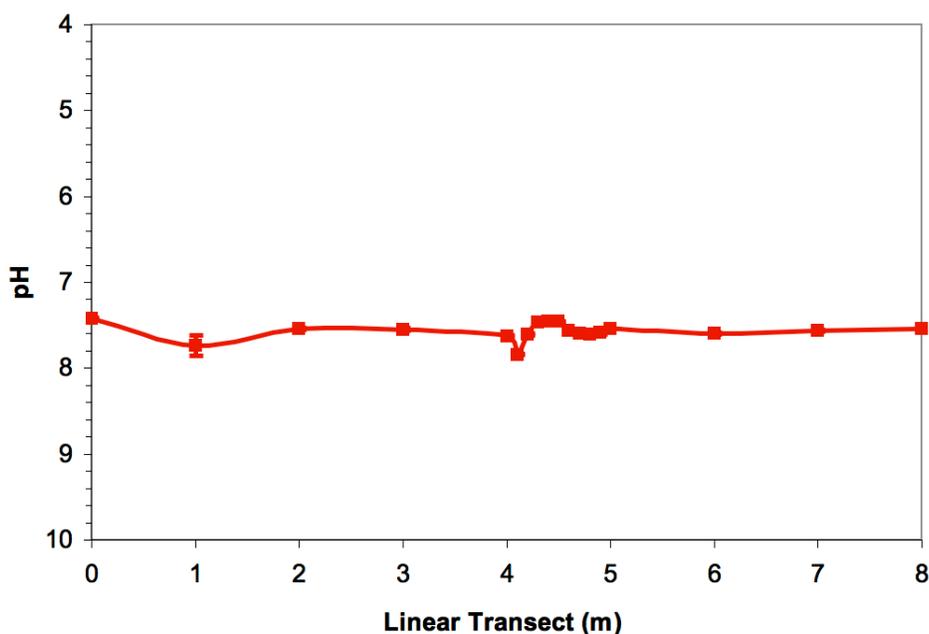


Figure 44: pH profile of Atacama Desert soil leachates from AT10 P. One gram of each soil was leached in five milliliters of 18.2 mΩ water for one hour then filtered before the pH was measured with a commercially available pH probe.

to 7.84. The pH range for these surface soils is comparable to the pH range of

soils collected from the previous studies of Atacama soils by Bagaley [100] and Quinn et al. [28]. Additionally, the pH of these surface soils was also similar to the pH of the surface soil (from 0-5 cm in depth) on Mars determined by the Wet Chemistry laboratory aboard the Phoenix Mars Lander of $\text{pH } 7.7 \pm 0.3$ (Chapter 1).

Conductivity: Solution electrical conductivity was determined for all soil samples leached one hour with a 1:5 (wt:vol) soil-to-water ratio using one gram of soil and five milliliters of $18.2 \text{ m}\Omega$ water using a commercial Orion conductivity probe. The conductivity probe was calibrated each day prior to analysis with solutions of $100 \mu\text{S}/\text{cm}$, $1413 \mu\text{S}/\text{cm}$ and $12.9 \text{ mS}/\text{cm}$ KCl. The cell constant varied from 0.552 to 0.560 over the course of this analysis.

Figure 45 depicts the conductivity of the two vertical pits, AT10 6 and AT10 OE, and the linear transect, AT10 P. For both pits and the linear transect, the shape of the conductivity profile is highly correlated to the shape of the profile of the most dominant, highest concentration ion in the pit. This same correlation was seen in the conductivity profiles for the soils analyzed from the McMurdo Dry Valleys (Chapter 2).

The conductivity of the Martian soil (at a depth of 0-5 cm) was determined by the conductivity sensor in WCL to be $1635 \pm 375 \mu\text{S}/\text{cm}$ at 25°C . Comparing the conductivity of the Martian soil to the conductivity of the Atacama soil required that the Atacama electrical conductivity be corrected to account for the difference in leaching ratios. The Martian soil was leached in 5-times more water (1:25 soil to water compared to 1:5 soil to water) therefore the when comparing these two measurements the electrical conductivity of the Atacama soil was divided by a factor of five. The electrical conductivity was thus shown to be an order of magnitude lower in all three locations in the

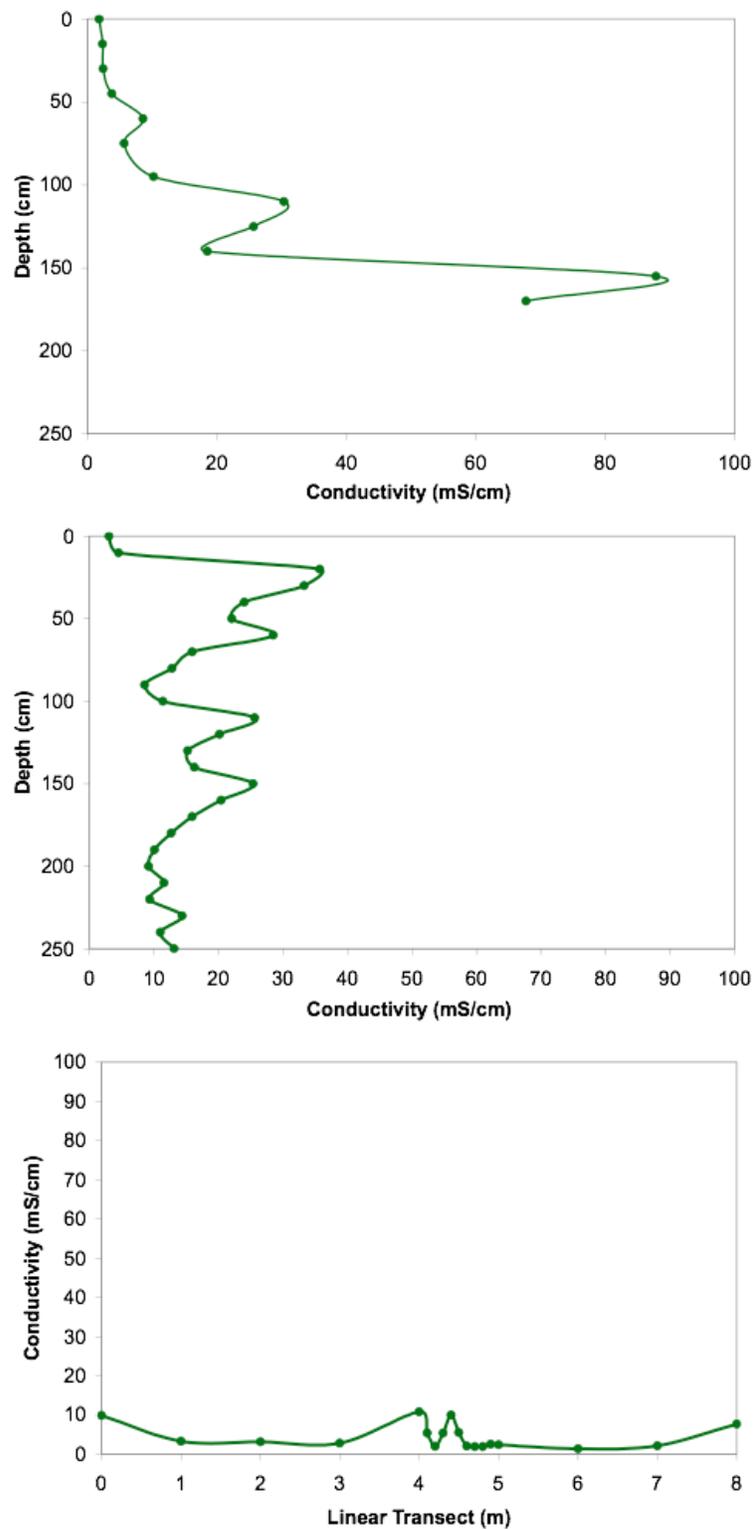


Figure 45: Electrical conductivity profiles of Atacama Desert soil leachates: Pit AT10 6 (on top), Pit AT10 OE (in middle) and Linear Transect AT10 P (on bottom). One gram of each soil was leached in 5 mL of 18.2 mΩ water for one hour then filtered before the conductivity was measured with a commercially available conductivity probe.

Atacama compared to Mars. The soil at location AT10 P was the closest in electrical conductivity to Mars averaging $884 \pm 627 \mu\text{S}/\text{cm}$.

The non-corrected conductivity results were then used to calculate the ionic strength of the soil leachate solutions (μ_m). The resulting ionic strengths calculated by this method could subsequently be compared to the ionic strengths determined from the IC and acid-base titration experiments (μ_{exp}). The results of the ionic strength calculations are discussed below.

Ionic Strength: The ionic strength of the soil leachate solutions from the soils collected in the Atacama were calculated using two methods: from the IC and acid-base titration data using Equation 7 (μ_{exp}) and from the measured solution conductivity using Equation 8 (μ_m) as discussed in Chapter 2. Figure 46 shows a comparison of ionic strengths as a function of depth or horizontal distance calculated by both methods for AT10 6, AT10 OE and AT10 P. For both pits and the linear transect, the $\mu_{exp} > \mu_m$. Once again, as seen from the analysis of soils from the stable upland zone in the McMurdo Dry Valleys, the slope used in the Griffn-Jurinak relationship (Equation 8) does not hold for soils from the Atacama Desert. As discussed in Chapter 2, the Griffn-Jurinak relationship holds for soil extracts dominated by monovalent ions, Cl^- and Na^+ . While the dominant cation in these soils was Na^+ , the dominant anion was not Cl^- . Instead the dominant anion was SO_4^{2-} which is divalent. Therefore, it has once again been shown the slope of the Griffn-Jurinak relationship requires modification when used in the analysis of soils from extreme environments.

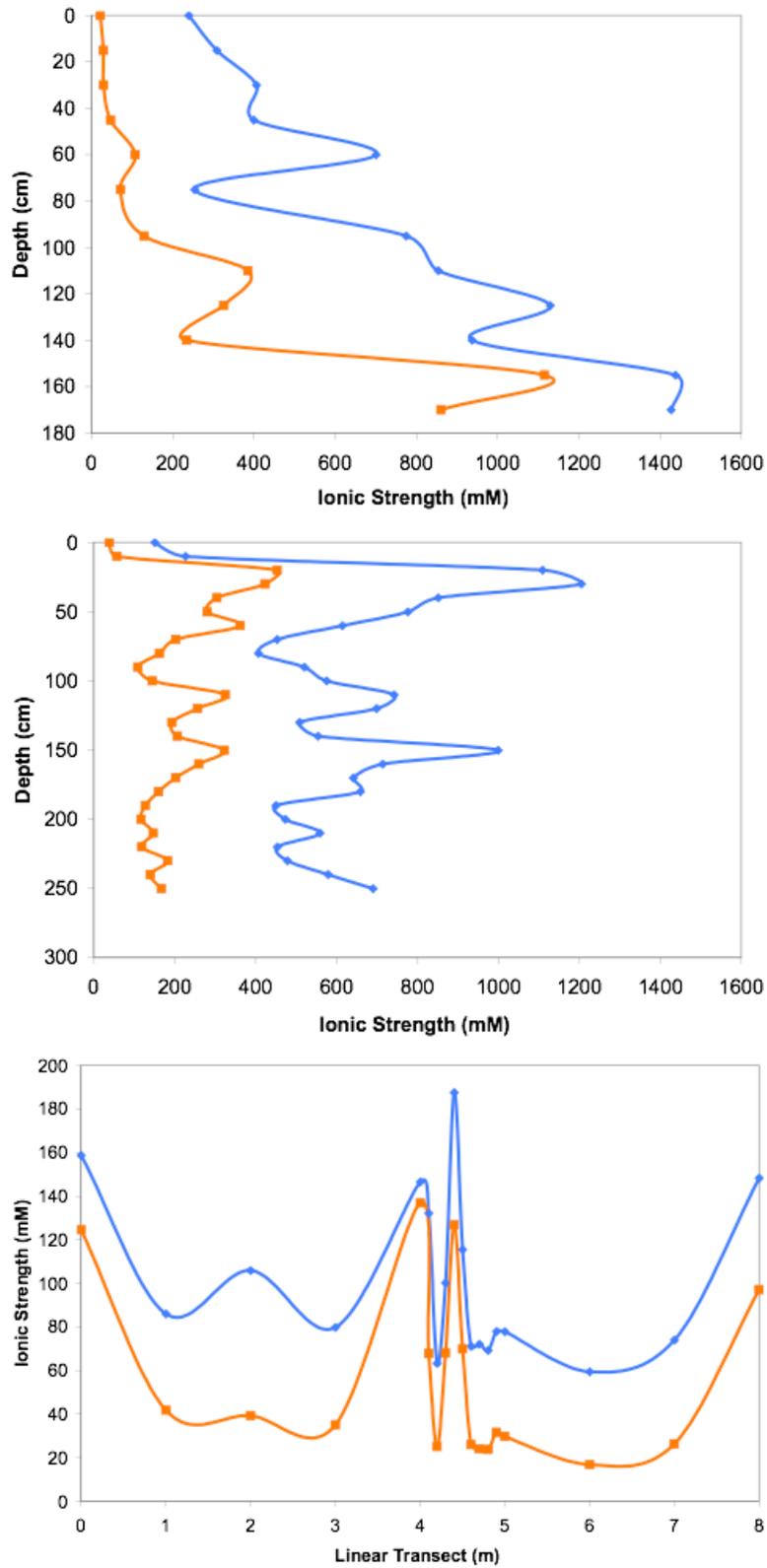


Figure 46: Ionic strength profiles of Atacama Desert soil leachates: Pit AT10 6 (on top), Pit AT10 OE (in middle) and Linear Transect AT10 P (on bottom) calculated by two separate methods: μ_{exp} (blue diamonds) and μ_m (orange squares).

4.4.5 Comparison of Atacama Soils to Martian Soil

Soil samples from three locations in the Atacama Desert were analyzed for soluble ion content, soil pH and conductivity. The results from this analysis were then compared to the results from the WCL analysis of the Martian soil at the Phoenix Lander site (see Chapter 1) to compare these two extreme environments. Table 33 compares the geochemical properties of the Martian soil determined by WCL to the soils from the three locations sampled in the Atacama Desert determined by ion chromatography. [51]

The soil properties for the Atacama are listed collectively for soils collected from the topsoil (i.e. top 5 cm), analogous to the depth of soil analyzed on Mars. For this reason there was only one soil sample from AT10 OE and AT10 6 in the Atacama. However, sampling in extreme environments is challenging and thus often limited. Comparison of only one or two samples, such as from Mars and these two locations in the Atacama, is not ideal but can still provide some interesting information. [51]

The pH of the Martian soil at the Phoenix Lander site most closely matched the pH of the soils from the location AT10 P, the linear transect. The soils from the other two locations, AT10 OE and AT10 6 were slightly more acidic than the Martian soil. The electrical conductivity of the Martian soil was within the same order of magnitude as the soils from all three locations in the Atacama. However, the conductivity was higher in all three locations in the Atacama indicating these soils were saltier than Mars. [51]

When comparing the individual soluble ions, Na^+ , Ca^{2+} , Cl^- , and SO_4^{2-} , were one to two orders of magnitudes higher in all locations in the Atacama Desert than was seen on Mars, while the soluble ions of Mg^{2+} and ClO_4^- was one or more orders of magnitude lower in all locations in the Atacama than on Mars. As for the other comparable ions, NH_4^+ , K^+ , and NO_3^- , there was some

Table 33: Comparison of soils from the north polar region of Mars to soils from three locations in the Atacama Desert

| Geochemical Property | Mars ^a (n = 2) | Atacama AT10 OE ^b (n = 1) | Atacama AT10 6 ^b (n = 1) | Atacama AT10 P ^b (n = 18) |
|---|---------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| pH | 7.7 ± 0.3 | 7.33 ± 0.01 | 6.21 ± 0.05 | 7.57 ± 0.10 |
| Conductivity (μS/cm) | 1635 ± 375 | 603 ± 3 ^c | 350 ± 0.4 ^c | 884 ± 627 ^c |
| Li ⁺ (mM) | N.D. ^d | N.D. ^d | 0.408 ± 0.017 | 0.022 ± 0.002 |
| Na ⁺ (mM) | 1.4 ± 0.3 | 148.3 ± 8.4 | 32.4 ± 5.0 | 67.4 ± 21.9 |
| NH ₄ ⁺ (mM) | N.D. ^d | 4.6 ± 1.3 | N.D. ^d | 0.85 ± 0.03 |
| K ⁺ (mM) | 0.39 ± 0.08 | 0.92 ± 0.05 | 1.21 ± 0.03 | 2.0 ± 0.3 |
| Mg ²⁺ (mM) | 3.3 ± 1.7 | 0.8 ± 0.0 | N.D. ^d | 0.85 ± 0.03 |
| Ca ²⁺ (mM) | 0.6 ± 0.3 | 17.7 ± 2.0 | 10.0 ± 2.5 | 13.9 ± 0.8 |
| Cl ⁻ (mM) | 0.47 ± 0.09 | 2.9 ± 0.7 | 8.8 ± 1.0 | 21.9 ± 1.9 |
| NO ₃ ⁻ (mM) | N.D. ^d | N.D. ^d | 0.1 ± 0.0 | 2.2 ± 0.2 |
| SO ₄ ²⁻ (mM) | 5.4 ± 0.78 | 17.6 ± 1.4 | 99.1 ± 1.9 | 12.0 ± 0.6 |
| ClO ₄ ⁻ (mM) | 2.4 ± 0.5 | 0.36 ± 0.09 | N.D. ^d | 0.0013 ± 0.0001 |
| [Na ⁺]:[K ⁺] | 2:1 to 6:1 | 144:1 to 180:1 | 22:1 to 32:1 | 20:1 to 53:1 |
| [Na ⁺]:[Mg ²⁺] | 1:1 to 6:1 | 175:1 to 196:1 | — | 52:1 to 146:1 |
| [Na ⁺]:[Ca ²⁺] | 1:1 to 5:1 | 7:1 to 10:1 | 2:1 to 5:1 | 3:1 to 7:1 |
| [Mg ²⁺]:[K ⁺] | 3:1 to 16:1 | 0.8:1 to 0.9:1 | — | 0.4:1 to 0.5:1 |
| [Mg ²⁺]:[Ca ²⁺] | 2:1 to 17:1 | 0.04:1 to 0.05:1 | — | 0.06:1 to 0.07:1 |
| [Mg ²⁺]:[Cl ⁻ + ClO ₄ ⁻] | 0.5:1 to 2:1 | 0.2:1 to 0.4:1 | — | 0.2:1 to 0.4:1 |
| [Ca ²⁺]:[K ⁺] | 0.6:1 to 3:1 | 16:1 to 23:1 | 6:1 to 11:1 | 6:1 to 9:1 |
| [Cl ⁻ + ClO ₄ ⁻]:[Na ⁺] | 1:1 to 3:1 | 0.02:1 to 0.03:1 | 0.2:1 to 0.4:1 | 0.2:1 to 0.5:1 |
| [Cl ⁻ + ClO ₄ ⁻]:[K ⁺] | 5:1 to 11:1 | 3:1 to 5:1 | 6:1 to 8:1 | 9:1 to 14:1 |
| [Cl ⁻ + ClO ₄ ⁻]:[Ca ²⁺] | 3:1 to 12:1 | 0.1:1 to 0.3:1 | 0.6:1 to 1:1 | 1:1 to 2:1 |
| [SO ₄ ²⁻]:[Na ⁺] | 3:1 to 6:1 | 0.1:1 to 0.1:1 | 3:1 to 4:1 | 0.1:1 to 0.3:1 |
| [SO ₄ ²⁻]:[K ⁺] | 10:1 to 20:1 | 17:1 to 22:1 | 78:1 to 86:1 | 5:1 to 7:1 |
| [SO ₄ ²⁻]:[Mg ²⁺] | 1:1 to 4:1 | 20:1 to 24:1 | — | 13:1 to 15:1 |
| [SO ₄ ²⁻]:[Ca ²⁺] | 5:1 to 21:1 | 0.8:1 to 1:1 | 8:1 to 14:1 | 0.8:1 to 1:1 |
| [SO ₄ ²⁻]:[Cl ⁻ + ClO ₄ ⁻] | 1:1 to 3:1 | 4:1 to 8:1 | 10:1 to 13:1 | 0.5:1 to 0.6:1 |

^a WCL ISE response when 1 cm³ of soil with assumed density of 1 g/cm³ was added to 25 mL of pure water

^b IC result of soil leachate solution when 1 g of soil was leached in 5 mL of pure water for 1 hour

^c The conductivity of the Atacama soils was corrected to account for the difference in leaching ratios between the Atacama soil and the Martian soil.

^d N.D. = Not Detected. The value were below the instrument's limit of detection for that ion

variation between the three locations in the Atacama. No NH_4^+ was detected on Mars or the location AT10 6 in the Atacama, while there were measurable quantities of NH_4^+ in the other Atacama locations. The concentration of K^+ was on the same order of magnitude on Mars and Atacama location AT10 OE, while the concentration of K^+ was an order of magnitude greater in the other two Atacama locations. [51] It was not possible to measure the concentration of NO_3^- on Mars due to the 10^3 -time greater sensitivity of the ISE to ClO_4^- over NO_3^- . However, from the measured conductivity of the solutions on Mars it can be estimated that the $[\text{NO}_3^-] \leq 1$ mM. [52] Using this estimate, the $[\text{NO}_3^-]$ was at least an order of magnitude higher in the location AT10 P, but may be on par with the concentrations seen in the other two locations. [51]

Finally, there were small but measurable concentrations of Li^+ at two of the locations in the Atacama, AT10 6 and AT10 P. It was assumed there would be no Li^+ present in the Martian soil, and thus a Li^+ ISE was chosen as a reference electrode. It should be noted that if the levels of Li^+ found in the Atacama at some locations were present in the Martian soil, it would have affected the WCL analysis and the resulting ions concentrations determined. [51]

In addition to comparing the concentrations of ions in the soils from these different extreme environments, the ratios of these ionic species were also compared. The range of ratios were calculated from the ion concentrations and corresponding standard deviations. There were a few similar ratios of ions in both the Martian soil and in the soil from one or more locations in the Atacama. Two ratios, $(\text{Cl}^- + \text{ClO}_4^-)/\text{K}^+$ and $\text{SO}_4^{2-}/\text{K}^+$, were similar at AT10 OE. Four ratios, $\text{Na}^+/\text{Ca}^{2+}$, $(\text{Cl}^- + \text{ClO}_4^-)/\text{K}^+$, $\text{SO}_4^{2-}/\text{Na}^+$ and $\text{SO}_4^{2-}/\text{Ca}^{2+}$, were similar at AT10 6 and two ratios; $\text{Na}^+/\text{Ca}^{2+}$ and $(\text{Cl}^- + \text{ClO}_4^-)/\text{K}^+$ were similar at AT10 P. Similar ratios indicate similar accumulation and depletion

pathways for the ions in both environments. However, most ratios were either higher or lower in the Atacama than on Mars indicating there are different mechanisms of accumulation and/or depletion of the ionic species occurring in these environments. [51]

Overall, there was a similar order of magnitude of the electrical conductivity of the soils from the Phoenix landing site on Mars and the three locations sampled in the Atacama Desert. However, the electrical conductivity was higher in all three locations in the Atacama and that was reflected in the higher concentrations of most, but not all, ions in the Atacama soils compared to the Martian soil. [51] This comparative study contradicted the long-standing proposal of similar concentrations of Cl^- , NO_3^- , SO_4^{2-} and ClO_4^- in the Atacama and on Mars [81], at least at this location on Mars. As for which location in the Atacama was most similar to Mars in ion concentrations, all three were comparable, but with only one sample at comparable depth taken from the locations AT10 6 and AT10 OE, it was difficult to make as strong case for either of these locations as for AT10 P. Large differences in the ratio of ionic species among the three locations in the Atacama and on Mars indicate that all four of these locations differ in their mechanisms of ion accumulation and depletion. [51]

4.5 Conclusions

The soils from the Atacama Desert have for a long time been considered by many to be the best analog soils to Mars. Soils from three locations across the Atacama, two pits and one linear transect, were analyzed by a variety of techniques including ion chromatography (IC), the ion selective electrodes (ISE) in WCL, and acid-base titration to determine the soluble ionic species present, with IC and acid-base titration being the more reliable methods. In

addition, the pH, conductivity and ionic strength of the soil leachate solutions were also determined. These results were then compared to the Martian soil at the Phoenix Lander site as determined by WCL.

In comparing the soils analyzed at three distinct locations through the Atacama, it was found that similar ions were present in all three locations: Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , ClO_4^- , HCO_3^- and SO_4^{2-} with Na^+ and SO_4^{2-} being the most abundant cation and anion in all three locations. Lithium, ammonium and carbonate were also present in measurable quantities in two locations, AT10 OE and AT10 P for Li^+ and NH_4^+ and AT10 OE and AT10 6 for CO_3^{2-} . In addition to the lack of measurable for Li^+ and NH_4^+ at location AT10 6, this pit also contained a layer of caliche blanco at a depth of 170 cm which was absent in the pit at location AT10 OE. The caliche blanco layer consisted of salt crystals of Na_2SO_4 (also known as mirabilite) which were identified by SEM-EDX.

When the Atacama soils were compared to the Martian soil from the Phoenix Lander site only the samples collected from a depth of 5 cm or less were used because the Martian soil analyzed was collected from the top 5 cm. of soil. This limited the comparison to only one soil sample each from AT10 6 and AT10 OE. However, sampling in extreme environments is challenging and thus often limited. Comparison of only one or two samples, such as from Mars and these two locations in the Atacama, is not ideal but can still provide some interesting information.

In comparing the Atacama soil to the Martian soil it was found there was similarity in soil pH and the conductivity (when corrected for the difference in leaching ratios) an order of magnitude lower in all three locations in the Atacama, with site AT10 P having the most similar conductivity to the Martian soil. Both the concentration of soluble ions and ratio of these ionic species were

compared. In comparing the ion concentrations it was found Na^+ , K^+ , NH_4^+ , Ca^{2+} , Cl^- , and SO_4^{2-} , were one or two orders of magnitudes higher in the Atacama Desert, while Mg^{2+} and ClO_4^- was one to three orders of magnitude lower. Since there was no way to measure the NO_3^- on Mars, an estimate of ≤ 1 mM was used. This is lower than the concentrations found in Atacama AT10 P but on par with the concentrations at the other two locations. In comparing the ion ratios, there were many differences not only among the soils from the three locations in the Atacama but also between the Atacama soils and the Martian soil. This indicated there were likely different mechanisms of soluble ion accumulation and depletions between all of these locations. [51]

Despite all of the apparent differences between the Atacama soils and the Martian soil, one must remember that not only are two different extreme environments being compared, but two different planets. Differences in ion concentrations were to be expected. The fact that the concentration of soluble ions in the soil in the north polar region on Mars at the Phoenix lander site and the soil from these three locations in the Atacama were within one or two orders of magnitude for most ions and within the three orders of magnitude for ClO_4^- and possess similar pH and electrical conductivity shows just how similar they are in terms of their geochemical properties. Like with soils on Earth, there is little evidence to support a hypothesis that the soil on Mars is homogeneous and therefore it is possible that other locations on Mars have soil with geochemical properties even more similar to the Atacama Desert soil studied herein. [51]

5 Effects of Soil Preparation on the Analysis of Soils from Extreme Environments

5.1 Introduction

The experimental methodology for the determination of soluble salts in extreme environments was investigated. There is no established method for the extraction of soluble salts from these types of environments. This leads to non-uniformity in sample analysis from one investigation to the next. This issue was first brought to light when analyzing the soils collected from the McMurdo Dry Valleys in Antarctica. Soil analysis of sample collected from 11 pits in the MDV was performed at Tufts University (Chapter 2). Duplicate analysis on Pits 2 and 7 was performed at Johnson Space Center (JSC) in Houston, Texas. Comparison of the soil profiles, the soluble ionic species present as a function of depth, compiled at Tufts and JSC revealed some noticeable differences (Figure 47).

While both the Tufts and JSC anion soil profiles were on the same order of magnitude, there was a large difference in the shape of their respective profiles. In the Tufts anion profile for Pit 7, Figure 47 (top), the $[\text{SO}_4^{2-}]$ decreased from the first soil horizon to the second and third and then increased back at the permafrost layer to approximately the same concentration as the first soil horizon, while the $[\text{Cl}^-]$ and $[\text{NO}_3^-]$ decreased continuously down the four soil horizons. In contrast, in the JSC anion profile, Figure 47 (middle), the concentrations of all three anions followed relatively the same pattern down the pit, slightly increasing in concentration for the first horizon to the second, then decreasing from the second to the third and slightly increasing from the third to the permafrost layer.

The discrepancy between the soil profiles led to comparing the analyti-

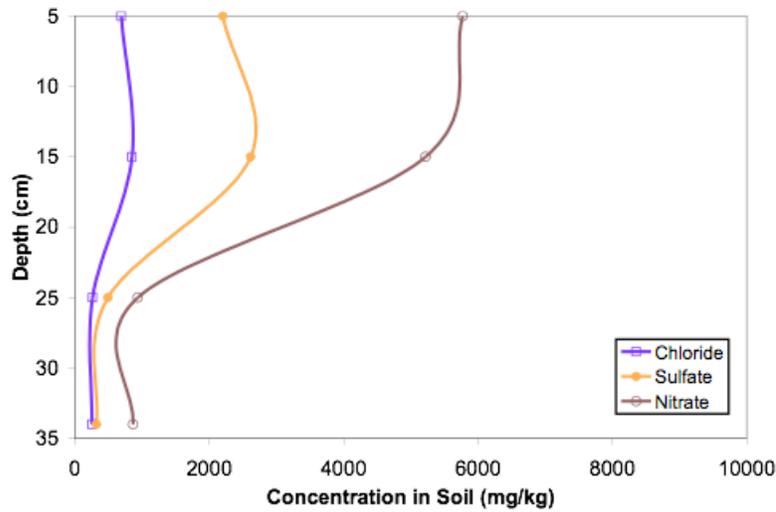
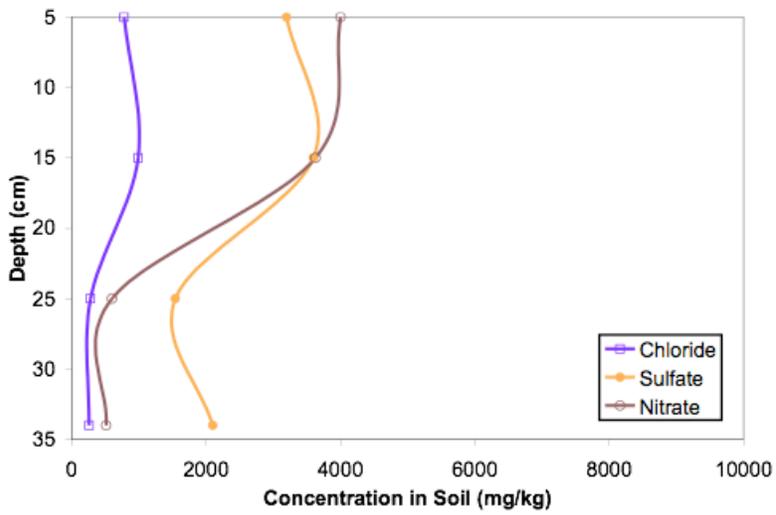
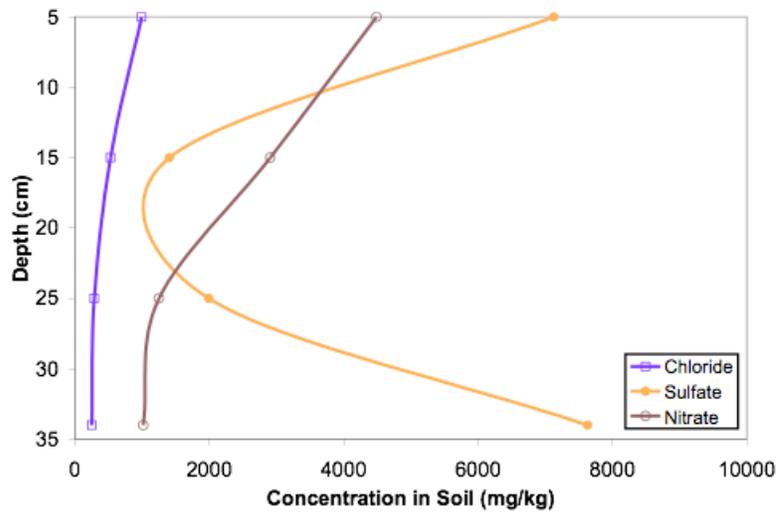


Figure 47: Difference in anion soil profiles of Pit 7 in University Valley as a result of different sample preparations: (Top) Tufts' analysis with parameters from Table 34, (Middle) JSC's analysis with parameters from Table 34, (Bottom) and Tufts' analysis using JSC parameters from Table 34

cal methods used by JSC and Tufts for the soil analysis. Table 34 lists the soil sample preparation performed by each institution. The two experimen-

Table 34: Comparison of soil preparation variables used by Tufts University and Johnson Space Center (JSC) for the analysis of ADV soils

| | Tufts | JSC |
|---------------------------|-------------------------------------|-------------------------------|
| Sample separation | Homogenization (mortar & pestle) | Sieved (2 mm screen) |
| Leaching solution | 18.2 mΩ water | 18.2 mΩ water |
| Leaching ratio | 1:25 (1 gram in 25 mL) | 1:1 50 grams in 50 mL) |
| Leaching time | 23 hours | 1 hour |
| Method of agitation | 30 seconds (by hand) | 1 hour (mechanical shaker) |
| Leaching temperature | Room temperature | Room temperature |
| Number of extractions | 1 | 1 |
| Filtering | 0.2 μm filter | 0.2 μm filter |
| Storage prior to analysis | Lab bench | Refrigerator |

tal methods were very different, with different sample separation techniques, leaching ratios, leaching times, agitation methods and even storage methods prior to analysis. The analysis of the soils from Pits 2 and 7 were repeated at Tufts using the same soil method as JSC and the results more closely matched (Figure 47 bottom), though there was still some difference in the overall concentrations of ions at each soil horizon. Therefore, it was determined the differences in sample preparation was the cause of the discrepancy between the results obtained at Tufts and JSC and highlights the importance of examining the different soil preparation variables and how each can affect the outcome of the analysis of soluble ionic species in soils from extreme environments.

This chapter discusses the different variables present in the preparation of soils for analysis which leads to the non-uniformity of sample analysis from one investigation to the next. Preliminary data as to how four of these variables, leaching time, leaching ratio, method of agitation and sample separation, affects the outcome of soluble ions as analyzed by ion chromatography is pre-

sented. A discussion follows as to the plans for a more in-depth study of the effects of sample preparation on the analysis of soils, especially those from extreme environments such as the McMurdo Dry Valleys of Antarctica or the Atacama Desert in Chile.

5.2 Background

Several variables need to be addressed in the preparation of soil samples for experimental analysis for soluble species. Sample preparation procedures vary widely in the literature. Therefore, it is necessary to determine how each preparation variable affects the final outcome of the sample analysis. Below each experimental variable is discussed along with its variations as seen in the literature in respect to the analysis of extreme environment soil samples.

5.2.1 Sample Separation

Separation of the sample so only particles of a certain size are to be analyzed allows sampling to be more consistent from one analysis to the next. Two different methods of sample separation are discussed, those used by Tufts and JSC in the analysis of soils from the MDV during the International Polar Year (Chapter 2). Each method is expected to lead to a different analytical result and the method chosen should depend on why the soil is being examined.

One method of sample separation is sieving. This was the method of sample separation used by JSC in the analysis of the soil from the MDV. The soil is put through a screen with 2 mm holes. The portion of soil material of 2 mm or less in size is collected for analysis, while the portion of soil measuring >2 mm is excluded from analysis. This method ensures consistent sample size and does not change the structure of the soil by exposing any new surfaces. The total soluble species present in the soil sample cannot be determined unless

the >2 mm portion of soil is also analyzed. Sieving is the most often used method of sample separation seen in the literature for the analysis of soils from extreme environments such as the Atacama [77, 97], and the McMurdo Dry Valleys [49, 101].

Another method to ensure consistent sampling is homogenization. This was the method of sample separation used by Tufts in the analysis of the MDV soil (Chapters 2 and 3). Homogenization is performed by pulverization of the soil with a mortar and pestle. Pulverization breaks apart larger sized particles in the soil into smaller particles <600 microns in size. Breaking apart larger particles in the soil exposes new surface area as well as any soluble species which may be present inside these larger particles. Thus, all of the soil collected can be leached and analyzed, nothing gets separated out and excluded from the analysis.

5.2.2 Leaching Solution

The solution used for leaching soil samples can affect the amount of soluble species which can leach from the soil into the solution. Aqueous solutions are always used for leaching soluble species. Water in varying forms of purity, such as distilled [32, 102], deionized [97, 101], and ultrapure 18.2 m Ω [73, 103], is the most commonly used solution for leaching soil samples. Though sometimes the purity level of the water is not specified [38, 49, 81] it is crucial the water is purified in some way to remove any ions present so there is no contribution of ions to the leachate from the water source.

For the analysis of certain soil samples, such as those known to have a high concentration of calcite, the leaching solution used will be acidified with an acid such as 1 or 2 M hydrochloric acid. [73, 77] The main reason for using of an acidified solution is to keep Ca²⁺ in solution between the start of

leaching and the actual leachate analysis. Samples with high levels of CaCO_3 can precipitate out Ca^{2+} during storage prior to analysis. Using HCl keeps the Ca^{2+} in solution and has not been shown to interfere with the analysis of other cations, Na^+ , K^+ , and Mg^{2+} , by ion chromatography when high levels of CO_3^- was present but can lead to poor peak resolution, irregular baseline, and peak broadening in samples with low levels of CO_3^- . [104]

The pH of the McMurdo Dry Valley soil samples collected during the International Polar Year (see Chapter 2) averaged 6.69 ± 0.14 . The leaching solution used by both Tufts and Johnson Space Center was 18.2 m Ω water. It was determined acidification was not necessary due to the already slightly acidic nature of the soil samples.

A specialized leaching solution was used in the analysis of Martian soil samples via ion selective electrodes (ISEs) in the Wet Chemistry Laboratory (WCL) aboard the Phoenix Mars Lander (see Chapter 1). The leaching solution was designated TS21 and consisted of 3×10^{-5} M to 1×10^{-3} M of several common anions and cations (see Table 2). This special leaching solution was used to allow for the determination of a calibration point for the ISEs prior to leaching the soil and was subtracted out to determine the concentration of ions as if leached in pure water. [5, 6] Using this leaching solution for other sample analyses is not recommended.

5.2.3 Leaching Ratio

Tufts used a 25:1 leaching ratio (25 mL of 18.2 m Ω water to leach 1 gram of soil) for the extraction of water-soluble species from the McMurdo Dry Valley soil samples collected during the International Polar Year (see Chapter 2) . This ratio was chosen to mimic the analysis conditions of the WCL aboard the Phoenix Mars Lander because these Antarctic samples were to be used

as a catalog in which to compare the Phoenix WCL results. However, the analysis at Johnson Space Center used a 1:1 leaching ratio (50 mL of 18.2 mM water to leach 50 grams of soil) for the extraction of water-soluble species for their analysis.

Many different water to soil leaching ratios have been seen in the literature for the leaching of soils including soils from extreme environments. These ratios include: 1:1 (JSC analysis), 5:1 [73, 102, 38, 49, 32], 20:1 [103, 77, 81], 25:1 [5], 40:1 [102], 100:1 [101, 97], and 500:1 [73]. The reasoning behind some of these water to soil leaching ratios is discussed below.

A 25 to 1 water to soil ratio for the extraction of water-soluble species was used for the analysis of soil samples on Mars by the WCL. [5] Each WCL cell was filled with 25 mL of TS21 leaching solution and 1 cm³ of soil (presumed to have a density of 1 g/cm³ and thus a weight of 1 gram) was added for analysis. The 25 mL of TS21 leaching solution was chosen, as this was the amount of water needed to fill the WCL cell beaker and ensure that all of the ISEs and other sensors inside the beaker were completely covered.

Looking at the literature for the analysis of Antarctic soils, it appears a 5:1 weight ratio of water to soil for leaching is most often used for the analysis all types of soil samples including those from the McMurdo Dry Valleys of Antarctica. [73, 102, 38, 49, 32] The 5:1 leaching ratio is in accordance with the method used for sodic and saline soils. [105] Examples for the usage of a 5:1 water to soil ratio include, Gibson et al. [32] who used this ratio for the analysis of soils from the Prespect Formation in Wright Valley as well as Bosckheim [38] who mapped the chemical and physical properties of 215 sites in the MDV including Taylor and Wright Valleys, the Asgard Range and the Quartermain Mountains in Arena and Beacon Valley as part of the McMurdo Valley Mapping Project (VALMAP).

However, it has been reported [97, 101] that using a 5:1 water to soil ratio can lead to incomplete salt extraction for extremely salt-rich soils like those likely to be found in Antarctica. For example, Bao et al. [101] determined that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is often not completely extracted using a 5:1 leaching ratio. Additionally, Bao et al. [101] has proposed the data from Gibson et al. [32] and Bockheim et al. [38] have underestimated the total water-soluble ion concentration in salt-rich zones. To overcome this problem, Bao et al. [101] used a repetition of three 100:1 water to soil extractions which ensured a greater than 99% extraction of all ions.

5.2.4 Leaching Time

For the McMurdo Dry Valley soil samples collected during the International Polar Year (see Chapter 2) two different leaching times were used. The samples analyzed by Tufts were leached for 23 hours. However, a leaching time of only one hour was used by Johnson Space Center.

Time of extraction (aka leaching time) of soluble species from soils varies widely in the literature. Extraction times of 30 minutes [102], 1 hour [77] (and JSC's analysis), less than 2 hours [102], 5 hours [103], 16 hours [97], 23 hours (Tufts' analysis), and 48 hours [32] have all been used. Currently there appears to be no standard length of time for leaching agreed upon for soil samples from extreme environments and no analyses have been performed to date which shows the effect of leaching time on sample analysis.

5.2.5 Sample Agitation

Another variable which can potentially have an effect on the type and concentration of soluble ions leached and therefore detected by ion chromatography is agitation during leaching. In the literature, several methods of agitation dur-

ing leaching have been reported. Samples have been shaken [102, 103, 73, 101], stirred magnetically [97] and sonicated [32]. Additionally, the bubbling of air or air with 1% CO₂ through the soil-water suspension has also been reported. [103] All of these techniques are designed to allow the leaching solution to better form a suspension with the soil which should allow more soluble material to leach from the soil into the leaching solution.

Two different methods of agitation were used in preparing the McMurdo Dry Valley soil samples collected during the International Polar Year (see Chapter 2) for analysis. The samples analyzed by Tufts were shaken for 30 seconds and then left undisturbed on the benchtop for the remainder of the leaching time. The samples analyzed by Johnson Space Center were agitated for the entire leaching time of one hour using a mechanical shaker.

5.2.6 Leaching Temperature

Leaching temperature is another variable to be considered in the preparation of soil samples. Since most papers do not specify the temperature at which the extraction of soluble species is performed, it is assumed extraction is performed at room temperature (20 or 25 °C). Temperature is known to affect solubility. Figure 48 shows the solubility curves for some common salts.

The solubility of most salts, for example NaNO₃ and (NH₄)₂SO₄, is increased as temperature increases from 0°C to 100°C. For some salts, such as KNO₃ the solubility change can be quite large (changing between 3.5 to 7.3 mass percent of solute for each increase of 10°C). Other salts, such as NaCl or CaSO₄, show hardly any change exhibiting a solubility which is fairly independent of temperature. There are even a few salts, such as Ce₂(SO₄)₃•9H₂O (not shown in Figure 48), which become less soluble with increasing temperature. Still other salts, such as Na₂SO₄ and MgSO₄, have a more complex

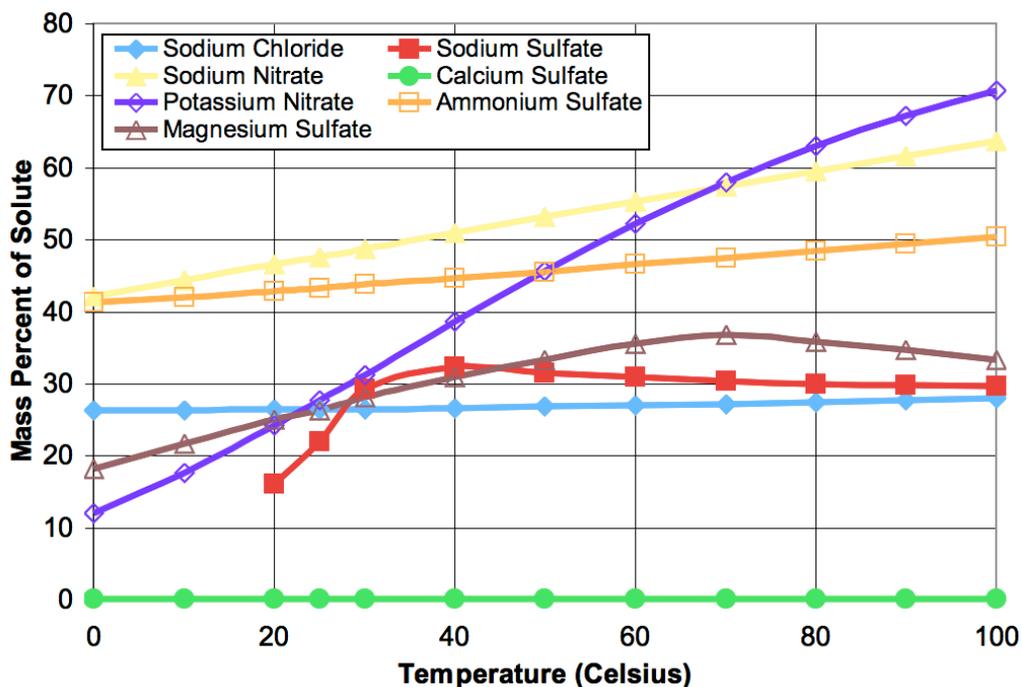


Figure 48: Aqueous solubility of inorganic salts at various temperatures [99]

relationship between temperature and solubility, increasing in solubility up to a given temperature (40°C and 70°C, respectively) and then beginning to decrease. Due to the complexity of temperature versus solubility relationships of different soluble salts, the temperature of extraction could potentially play a large role in the results of the analysis of soils from different environments.

5.2.7 Number of Extractions

The number of times a soil is extracted may also have an effect on the concentration of water-soluble species detected. In a majority of analyses soil samples are only extracted a single time [32, 38, 77, 49, 81, 102]. However, multiple extractions, of 2 or 3 times [73, 97, 101], or as many as 12 times [103], have been performed on soils from extreme environments.

More extractions allow for additional ions to leach from the soils into solution which would otherwise not be analyzed. In fact, it is known that the

entire concentration of the water-soluble sulfate in a soil sample with high sulfate content like those found in the Atacama cannot be extracted when a single extraction is used. It takes three extractions, at a $\sim 500:1$ water to soil weight ratio to retrieve $>99\%$ of the water-soluble sulfate from the soil. [73] This is just a single example of how the number of extractions affects the results from the analysis of extreme environment soils.

5.2.8 Storage Prior to Analysis

Ideally, the leachate from a soil sample should be analyzed as soon as possible after filtration. For this reason, papers typically do not discuss the method of storage used prior to analysis. However, sometimes it is necessary to store the leachate for a period of time prior to analysis. In the case of the two analyses performed by Tufts University and JSC on soil samples from the McMurdo Dry Valleys, storage of the samples prior to analysis was necessary. As seen in Table 34, the samples at Tufts were stored on the lab bench at room temperature ($\sim 25^\circ\text{C}$) until analyzed, while the samples from JSC were stored in the refrigerator. As with the temperature during leaching, the temperature during storage prior to analysis could have an effect on the final analysis result. As discussed in Section 5.2.6, solubility of certain species is dependent upon temperature, with most species becoming less soluble as the temperature is decreased, meaning it is possible that storage below a critical temperature could cause certain species to precipitate out of solution and not be detected when the analysis is finally performed. Therefore, the method of storage prior to analysis is another variable which needs to be considered.

5.3 Experimental

There are many different variables which can have an effect on the outcome of the analysis of soils from extreme environments including: sample separation, leaching solution, leaching ratio, leaching time, method of agitation, leaching temperature, number of extractions, and storage prior to analysis. A preliminary analysis was performed to determine the effect of four of these variables, leaching time, leaching ratio, method of agitation and sample separation to see how each affected the concentration of soluble ions detected. These four variables differed in the analysis of the MDV soils performed by JSC and Tufts. Also, the leaching time, leaching ratio and sample separation differed in the analysis of soils from Mars (Chapter 1), the MDV (Chapters 2 and 3) and the Atacama Desert (Chapter 4) in this work. One McMurdo Dry Valley soil sample from Pit 7 in University Valley, ANUV0727, was chosen for this preliminary work. The experimental procedure for each variable tested is discussed below.

5.3.1 Effect of Leaching Time

To determine the effect of leaching time on the concentration of soluble ions detected by ion chromatography, the soil sample, ANUV0727, was first homogenized by mortar and pestle. One gram of homogenized soil was added to 25 mL of 18.2 m Ω water (for a 25:1 weight ratio of water to soil), shaken for 30 seconds and leached for various lengths of time. After the desired leaching time, the sample was filtered through a 0.2 μ m filter and stored in an air-tight container on the benchtop in the laboratory at room temperature until analyzed. A total of nine different leaching times were tested: ten minutes, one hour, 23 hours, 48 hours (two days), 72 hours (three days), 216 hours (nine days), 504 hours (three weeks) and 672 hours (one month). The leachate so-

lutions were run in triplicate using the procedure for IC analysis outlined in Chapter 2.

5.3.2 Effect of Leaching Ratio

To determine the effect of leaching ratio on the concentration of soluble ions detected by ion chromatography, the soil sample, ANUV0727, was first homogenized by mortar and pestle. One gram of homogenized soil was added to various amounts of 18.2 m Ω water, shaken for 30 seconds and leached for 23 hours. After 23 hours, the sample was filtered through a 0.2 μ m filter and stored in an air-tight container on the benchtop in the laboratory at room temperature until analyzed. A total of six different leaching ratios of water to soil were tested: 5:1, 10:1, 25:1, 50:1, 100:1 and 250:1. The samples were run in triplicate using the procedure for IC analysis outlined in Chapter 2.

5.3.3 Effect of Agitation

To determine the effect of agitation on the concentration of soluble ions detected by ion chromatography, two different methods of agitation were examined. In Agitation Method 1, the soil-water solutions were hand shaken for 30 seconds then placed on the benchtop where they were allowed to leach undisturbed for the remainder of the leaching time. In Agitation Method 2, agitation for the entire leaching time was achieved by placement of the soil-water solution on a mechanical shaker. For both methods of agitation the soil sample was first homogenized by mortar and pestle, leached, filtered through a 0.2 μ m filter and stored in an air-tight container on the benchtop in the laboratory at room temperature until analyzed. The samples were run in triplicate using the procedure for IC analysis outlined in Chapter 2.

When testing the effects of agitation, two other variable were also simul-

taneously explored: leaching time and leaching ratio. Previously, soil samples were tested for the effects of leaching time (ten minutes, one hour, 23 hours, 48 hours, 72 hours, nine days, three weeks, and one month) using Agitation Method 1. Therefore, to test Agitation Method 2, samples of the same water:soil ratio (25:1 weight ratio) were leached using 18.2 mΩ water for ten minutes, 1 hour, 4 hours, 7 hours, 23 hours and 48 hours while being shaken for the entire time on a mechanical shaker. Only the shorter leaching times were chosen for this preliminary examination so IC analysis could be performed quicker, without the need to wait an entire month (as was done in the leaching time study) to determine the effect of a different agitation method. Additionally, soil samples were previously tested for the effect of leaching ratio (5:1, 10:1, 25:1, 50:1, 100:1 and 250:1 weight ratio) using Agitation Method 1. Therefore, samples were leached for 23 hours, using 18.2 mΩ water, with water to soil ratios of 5:1, 25:1, and 100:1 and Agitation Method 2 to compare the effect of leaching ratio with this second agitation method.

5.3.4 Effect of Sample Separation

To determine the effect of sample separation on the concentration of soluble ions detected by ion chromatography, the sample was separated in two ways. In Sampling Method 1, the sample was homogenized via mortar and pestle. In Sampling Method 2, the sample was sieved for particles less than 2 mm in size. For both separation methods, one gram of the separated soil (either homogenized or sieved) was added to 25 mL of 18.2 mΩ water (for a 25:1 water to soil weight ratio) and leached for 23 hours with Agitation Method 1. After 23 hours the sample was filtered through a 0.2 μm filter and stored in an air-tight container on the benchtop in the laboratory at room temperature until analyzed. The samples were run in triplicate using the procedure for IC

analysis outlined in Chapter 2.

5.4 Results and Discussion

The results from the study of the effects of leaching ratio, leaching time, method of agitation, and sample separation are discussed below. For each study only a single soil sample from the McMurdo Dry Valleys, ANUV0727, was analyzed. These results are only preliminary and more analyses must be performed to verify these findings. This preliminary analysis was meant as a jumping off point for a future more in-depth study.

5.4.1 Effect of Leaching Time

Nine different leaching times, from ten minutes to one month were used to extract water-soluble ions from one representative MDV soil sample, ANUV0727. Each sample used the same leaching ratio of 25:1 water to soil and was leached for the set time before being filtered and analyzed by IC to determine if leaching time had any effect on the concentration of soluble ions leached from the soil. Figure 49, shows the concentration of each ion in the soil (in mg/kg) as a function of leaching time (in days).

Five cations, Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} , and three anions, Cl^- , NO_3^- , and SO_4^{2-} , were detected for all nine leaching times. The concentration of each ion detected by IC was consistent for all nine leaching times tested, within the standard deviation of the three sample aliquots. Therefore, from this preliminary study it has been shown that leaching time alone has little to no effect on the concentration of ions leached into solution and subsequently detected.

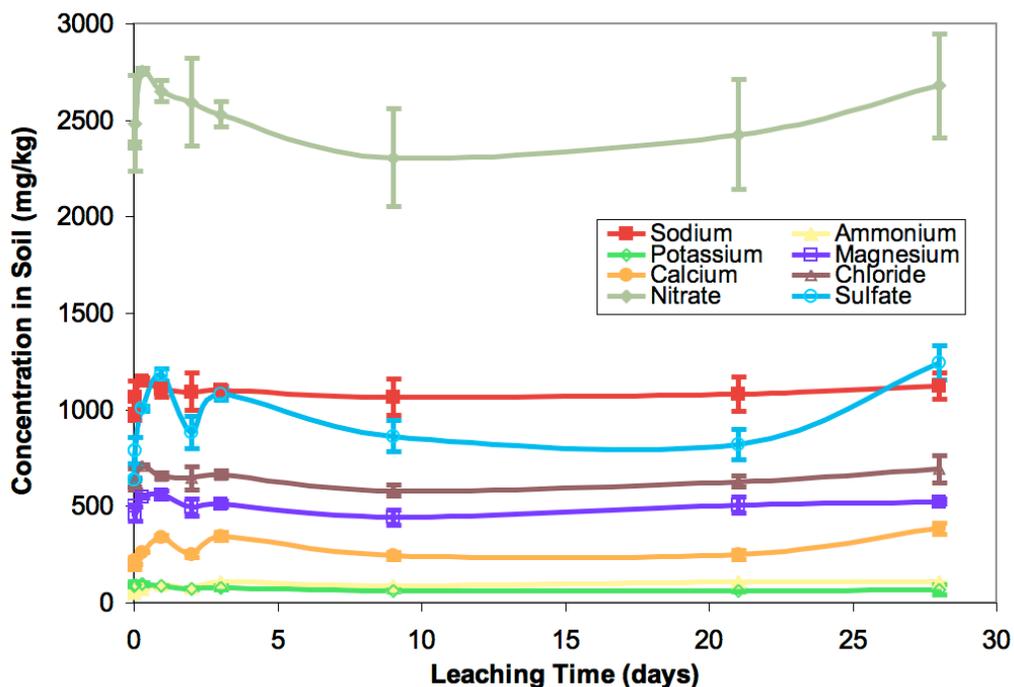


Figure 49: Plot of Leaching time (in days) versus concentration of ions in soil (in mg/kg) for MDV soil sample ANTV0727. The soil was prepared for analysis by adding 1 gram of homogenized soil to 25 mL of 18.2 mΩ water, shaking for 30 seconds and leaching for 10 minutes to 672 hours (1 month) at room temperature. The leachate was filtered and run in the IC.

5.4.2 Effect of Leaching Ratio

Six different leaching ratios of water to soil, from 1:1 to 250:1, were used for the extraction of water soluble ions from one representative MDV soil sample, ANUV0727. Each different water to soil ratio was leached for 23 hours, then filtered and analyzed by IC to determine if leaching ratio had any effect on the concentration of soluble ions leached from the soil. Figure 50, shows the average concentration of each ion in the soil (in mg/kg) as a function of the milliliters of water used to leach one gram of soil.

Regardless of the leaching ratio used, the same five cations, Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} , and three anions, Cl^- , NO_3^- , and SO_4^{2-} , were detected. However, there was some difference in the amount of each ion which leached

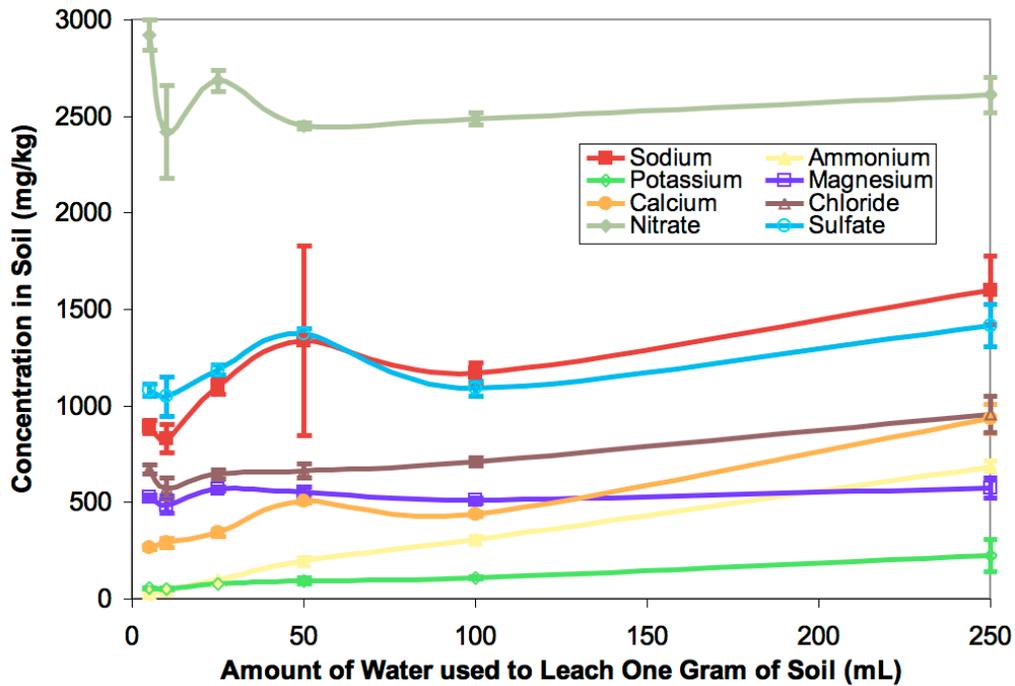


Figure 50: Plot of the milliliters of water used to leach one gram of soil versus concentration of ions in soil (in mg/kg) for MDV soil sample ANUV0727. The soil was prepared for analysis by adding 1 gram of homogenized soil to either 5 to 25 mL of 18.2 mΩ water, shaken for 30 seconds and leached for 23 hours at room temperature. The leachate was filtered and run in the IC.

into solution. When the water to soil ratio was $\leq 100:1$ water to soil, the concentration of each ion was consistent. As the ratio of water to soil increased above 99%, considerably more Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Cl^- were detected by IC meaning that more of these ions were leached into solution when using a water to soil ratio of 250:1. The concentrations of Mg^{2+} , NO_3^- , and SO_4^{2-} were not affected by changing the water to soil ratio and stayed consistent throughout. From this preliminary analysis, it was found that leaching ratio can have some effect on the amount of each ion leached into solution. Leaching ratios of 100:1 or less soil to water leached roughly the same amount of ions into solution, while a larger 250:1 ratio allowed more of some ions (Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Cl^-) to leach into solution. In fact, an additional 890:1 water to

soil ratio was subsequently analyzed and even more ions leached into solution with this even greater water to soil ratio.

5.4.3 Effect of Agitation

Soil samples were leached with two different methods of agitation, shaking for the first 30 seconds only (Agitation Method 1) and shaking the entire time on a mechanical shaker (Agitation Method 2) to determine if the method of agitation had an effect on the concentration of ions leached into solution. The method of agitation was also coupled with another variable, either leaching time or leaching ratio. The effects of both leaching time and leaching ratio with Agitation Method 1 have been previously discussed so only the results of leaching time and leaching ratio with Agitation Method 2 are discussed below.

The representative MDV soil sample, ANUV0727, was leached in a 25:1 water to soil ratio for 10 minutes, 1 hour, 4 hours, 7 hours, 23 hours and 48 hours before being filtered and analyzed by IC to determine if leaching time with agitation Method 2 had any effect on the concentration of soluble ions leached from the soil. Figure 51, shows the concentration of each ion in the soil (in mg/kg) as a function of leaching time (in days). As with Agitation Method 1, the same five cations, Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} , and three anions, Cl^- , NO_3^- , and SO_4^{2-} , were detected at all leaching times and the concentration of ions leached was not affected by the leaching time. A comparison of Figure 49 to Figure 51 shows the concentration of each ion leached at each time was comparable for all ions, except Ca^{2+} and SO_4^{2-} , by both agitation methods. There was a higher concentration of Ca^{2+} and SO_4^{2-} in the soil when leaching time was coupled with agitation suggesting that additional anhydrite (CaSO_4) or gypsum ($\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$) was able to leach into solution when agitated regardless of the time the sample was leached.

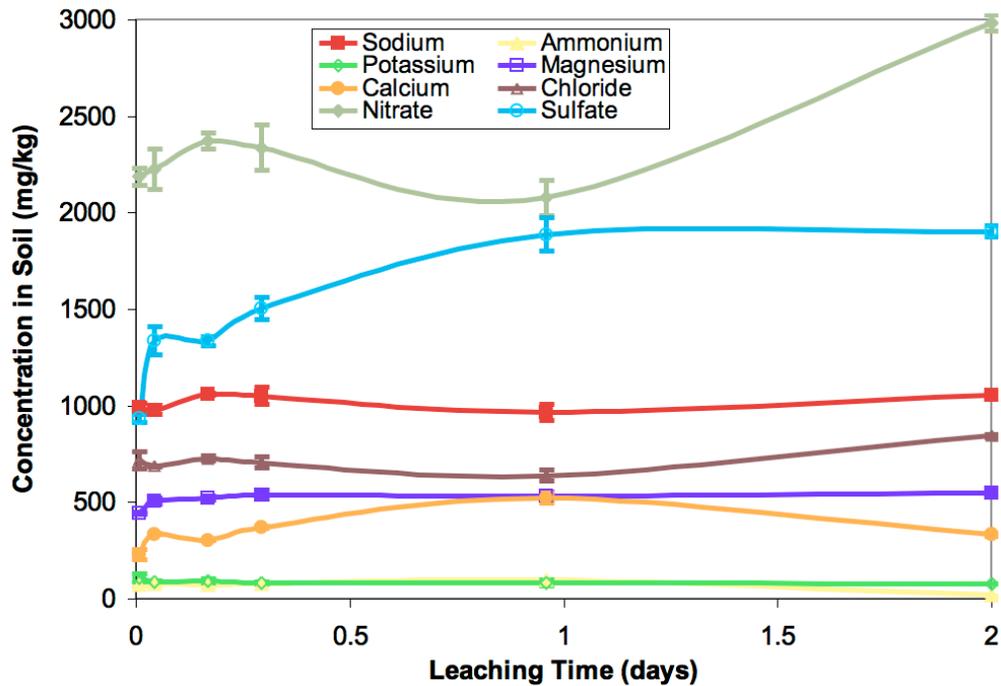


Figure 51: Plot of Leaching time (in days) versus concentration of ions in soil (in mg/kg) for MDV soil sample ANUV0727. The soil was prepared for analysis by adding one gram of the homogenized soil to 25 mL of 18.2 mΩ water, shaking with a mechanical shaker for 10 minutes to 48 hours (2 days) at room temperature. The leachate solution was filtered and run in the IC.

The representative MDV soil sample, ANUV0727, was leached for 23 hours at water to soil ratios of 5:1, 25:1 and 100:1 before being filtered and analyzed by IC to determine if leaching ratio with agitation Method 2 had any effect on the concentration of soluble ions leached from the soil. Figure 52 shows the concentration of each ion in the soil (in mg/kg) as a function the milliliters of water used to leach one gram of soil. As with Agitation Method 1, the same five cations, Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} , and three anions, Cl^- , NO_3^- , and SO_4^{2-} , were detected at all leaching ratios. However, the concentration of ions leached from each water to soil ratio were drastically different. The more water used to leach the one gram of soil, the greater the concentration of all ions leached into solution. This was similar to the result seen in Agitation Method

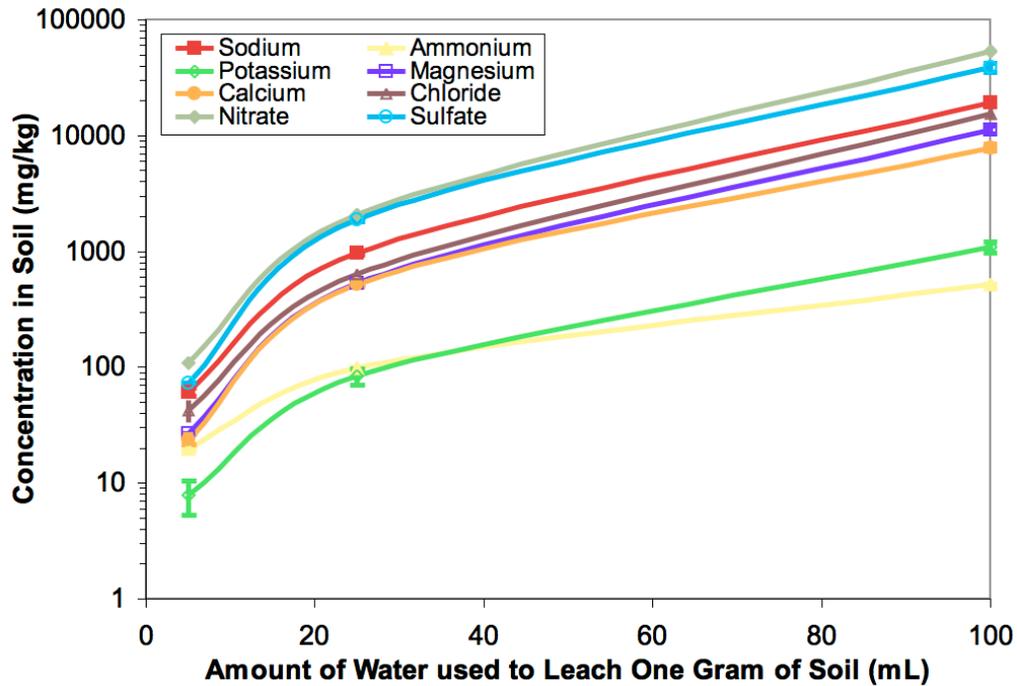


Figure 52: Plot of the milliliters of water used to leach one gram of soil versus concentration of ions in soil (in mg/kg) for MDV soil sample ANUV0727. The soil was prepared for analysis by adding 1 gram of the homogenized soil to 5 to 100 mL of 18.2 mΩ water and shaking with a mechanical shaker for 23 hours at room temperature. The leachate was then filtered and run in the IC.

1 (Figure 50) but much more pronounced. Therefore, it has been shown that the agitation method can have an effect on the amount of soluble ions leached into solution with more ions leached into solution with continuous agitation (Agitation Method 2) and this effect can be magnified with an increased water to soil ratio.

5.4.4 Effect of Sample Separation

Two different methods of separating soil samples for analysis were compared using the representative soil, ANUV0727. In Sampling Method 1 the soil bulk was homogenized via mortar and pestle to particles <600 microns, while in Sampling Method 2 the soil was sieved for particles less than 2 mm in size.

Each method used a leaching time of 23 hours, a leaching ratio of 25:1 water to soil weight ratio, and agitation method 1. Samples were then filtered and analyzed by IC to determine if the method of sample separation had an effect on the concentration of soluble ions leached from the soil into solution. Figure 53 shows a comparison of the concentration of soluble ions in the soil when separated prior to IC analysis with both methods.

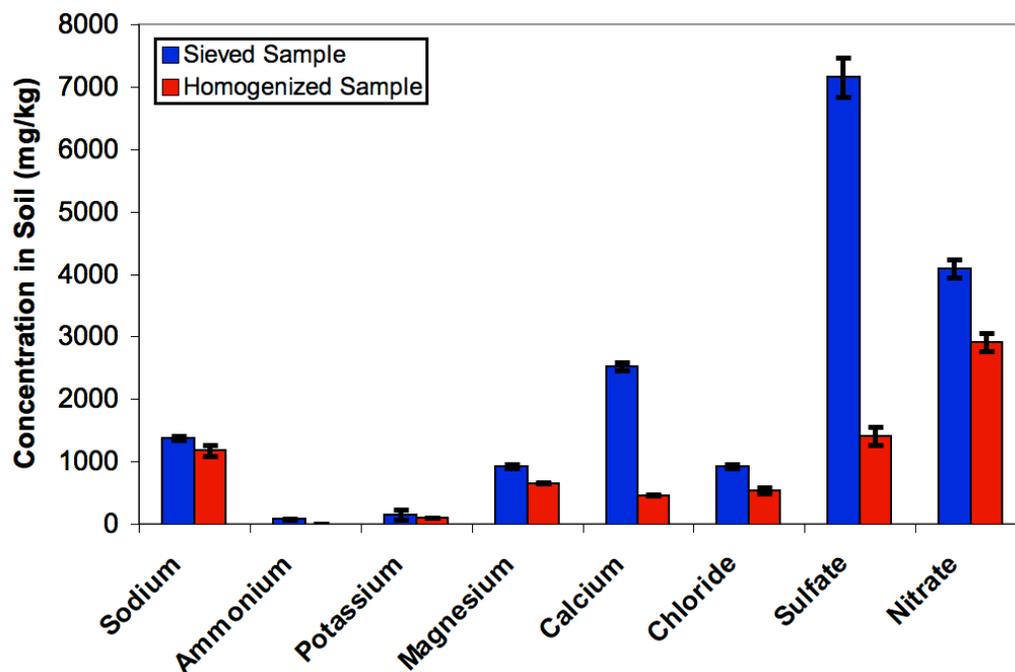


Figure 53: Comparison of ion concentration (in mg/kg) in a sample of the MDV soil ANUV0727 separated by two different methods: homogenization and sieving. The soil was prepared for analysis by adding 1 gram of either homogenized or sieved soil to 25 mL of 18.2 mΩ water, shaken for 30 seconds and leached for 23 hours at room temperature. The leachate was then filtered and run in the IC.

The soil for both separation methods leached out the same five cations: Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} and the same three anions: Cl^- , NO_3^- and SO_4^{2-} . However, there was a noticeable difference in the concentrations between the two methods. A higher concentration of each ion was leached into solution and was subsequently detected when prepared with Sampling

Method 2 than with Sampling Method 1 with the exception of K^+ in which the concentrations slightly overlapped. Some of the largest differences in concentrations were seen for NH_4^+ , where 20 times more was leached into solution with Sampling Method 2 as well as Ca^{2+} and SO_4^{2-} where five times more of each ion was leached into solution with Sampling Method 2. Since five times more Ca^{2+} and SO_4^{2-} was seen with Sampling Method 2 this suggests it was additional anhydrite ($CaSO_4$) or gypsum ($CaSO_4 \bullet 2H_2O$) which was able to leach into solution with this method. Overall, the total concentration of ions leached into solution with Sampling Method 2 was two times greater than the total concentration of ions leached into solution with Sampling Method 1.

The overall higher concentration of ions leached into solution from the sample separated using Sampling Method 2 can be explained as follows: the soluble salts present in the bulk soil sample were $<2mm$ in size or are loosely bound $>2mm$ and were easily broken down with minimal force with little to no additional soluble salts trapped in larger particles. When the sample was sieved to remove particles >2 mm, mostly minerals, containing little to no soluble salts were separated for the sample, leaving behind a higher ratio of soluble salt to other materials present in the sample to be analyzed. In contrast, when the bulk sample was homogenized in Sampling Method 1, larger materials containing little to no additional soluble salts were broken down creating a lower ratio of soluble salts to other materials present in the sample to be analyzed. Sieving soils concentrated the amount of soluble salts in the soil while homogenizing diluted the amount of salts in the remaining soils, therefore, causing the difference in ion concentrations for the two sampling methods seen in Figure 53.

From this preliminary study, it has been shown that sample separation can have an effect on the concentration of ions leached into solution for analysis.

In this case, Sampling Method 2 increased the overall concentration of each ion leached into solution and doubled the overall concentration of ions leached into solution as compared to Sampling Method 1. However, it has been proposed that analyzing the >2 mm soil portion excluded from the sieving process and combining the findings with the <2 mm data would result in a similar concentration of ions present in the original soil seen by the homogenization method. Further analysis of a variety of soil samples is necessary to confirm the finding presented herein and to determine if/how the results would change with the analysis of the >2 mm soil portion currently excluded from Sampling Method 2.

5.5 Conclusions

The experimental method for the preparation of soil samples for chemical analysis varies widely in the literature. However, it has been shown that differences in sample preparation can lead to differences in the results obtained from the subsequent analysis. One example of such differences was seen in the results of the analysis of soils from the McMurdo Dry Valleys of Antarctica analyzed by Tufts University and Johnson Space Center (Figure 47) using two vastly different sample preparations (Table 34).

Eight different sample preparation variables have been identified: separation, leaching solution, leaching ratio, leaching time, leaching temperature, agitation, number of extractions, and method of storage. Of these variables, preliminary studies were performed to determine the effects of four, separation, leaching ratio, leaching time, and agitation, on the subsequent analysis results for the concentration of soluble ions present both in the leachate solution (results not shown) and the original soil sample (Figures 49, 50, 51, 52 and 53). While only one soil sample was chosen for these preliminary tests it was

possible to determine which of these variables warranted further investigation.

Of the four variables tests, leaching time was shown to have the smallest effect on the concentration of soluble ions seen in both the leachate solution and the original soil sample, with no considerable change in concentration of any of the ions whether the soil was leached for as little as ten minutes or as long as one month. Additionally, adding agitation during leaching did not change this finding. This suggests that all of the salts present in this soil sample were highly soluble, dissolving quickly into solution, and any additional minerals present were not soluble under these conditions. However, this may not be the case with all soils and therefore even though leaching time had no effect on this sample it should still be investigated further with additional soil samples.

Leaching ratio, or the water to soil ratio used to leach the sample, was shown to have some effect on the concentration of ions detected in the leachate solution. This result is as expected because less water results in a more concentrated solution. When comparing the concentration of ions in the soil itself, there is a correction for the difference of water added during leaching. Thus, concentration of ions detected in the soil itself was less affected by the leaching ratio. In fact, up to a leaching ratio of 100:1 water to soil, there was no considerable difference in concentration of ions detected in the soil. Samples leached in >100:1 water to soil resulted in the detection of a higher concentration of some ions in the soil.

When the water:soil ratio was examined in conjunction with sample agitation during leaching, a different effect was observed. The concentration of each ion in the leachate solution decreased with increased soil-to-water ratio. This trend was intensified when looking at the concentration of each ion in the original soil sample. The change in concentration was large with a roughly

2 to 3 order of magnitude greater concentration of ions seen when leached in 100:1 water to soil with agitation than when leached in 5:1 water to soil with agitation. Therefore, has been shown from analysis of a single sample that leaching ratio in conjunction with agitation has an effect on analysis results and should definitely be explored further with additional soil samples.

The method of sample separation was also shown to affect analysis results. Sieving the sample leached more ions into the leachate solution than homogenization of the soil sample. The sieving method was also shown to result in a higher concentration of ions in the original soil sample. However, this result was as expected and it has been suggested that analyzing the >2 mm soil portion excluded from the sieving process and combining the findings with the <2 mm data would result in a similar concentration of ions present in the original soil seen by the homogenization method.

From this preliminary analysis it was shown that leaching time and leaching ratio when not combined with agitation do not have any considerable effect on the concentration of ions leached into solution and subsequently detected. Therefore, the differences in the sample preparation variables seen in this work, in the analysis of the soils from Mars (Chapter 1), the McMurdo Dry Valleys (Chapters 2 and 3) and the Atacama Desert (Chapter 4), would not significantly affect the ability to directly compare of the results. The sample separation was shown to have an effect on the concentration of ions leached into solution and subsequently detected, with the sieved soils having a greater overall concentration of ions leached into solution and subsequently detected. However, the difference in concentration was less than one order of magnitude. Therefore, even though the soils from the McMurdo Dry Valleys (Chapters 2 and 3) were homogenized while the soils from Mars (Chapter 1) and the Atacama Desert (Chapter 4) were sieved, the difference in separation

method does not affect the ability to directly compare these results.

From this preliminary analysis, it was shown that the different methods of soil preparation for soils from Mars, the McMurdo Dry Valleys, and the Atacama Desert did not affect the ability to directly compare these results. However, some soil preparation variables (*i.e.*, leaching ratio with agitation) did drastically change the concentration of ions leached into solution and subsequently detected. Therefore, a need was shown for a standardized method of soil analysis for soils from extreme environments. From this preliminary work, it is not possible to draw any conclusions as to the best sample preparation method for the analysis of soils of this type. A plan for an in-depth analysis of the effects of sample preparation on the analysis of soils, specifically soils from extreme environments is outlined below.

5.6 Future Directions

A preliminary study was performed to determine the effects of separation technique, leaching time, leaching ratio, and agitation during leaching on the amount of soluble ions leached into solution as subsequently analyzed by ion chromatography to determine concentration of ions in the leachate solution as well as concentration of ions in the original soil sample. This study used a single soil, ANUV0727, collected from the 9-20 cm soil horizon of Pit 7 in University Valley, a valley in the stable upland zone of the McMurdo Dry Valleys of Antarctica. The results from this study were used as a starting off point for the following proposed in-depth study of the effects of sample preparation on the analysis of soils, specifically soils from extreme environments, in attempts to standardize a method of soil sample preparation for these types of soils.

Choosing an appropriate subset of soil samples for this analysis is critical. A minimum of 10 to 15 soil samples should be analyzed to provide the nec-

essary diversity. The subset of soils must be suitably diverse to allow for the determination of parameters which would work well for the variety of different soils to ultimately use this standardized method. Soil samples must therefore be tested from a variety of different extreme environments, including but not limited to the Atacama Desert, McMurdo Dry Valleys, and Death Valley in California. Likewise, soils must be analyzed from different zones within each environment, such as each of the three microclimate zones in the MDV, as well as from different locations within each zone, such as the topsoil and at decreasing depths.

All eight of the sample preparation variables discussed in the background section, sample separation, leaching solution, leaching ratio, leaching time, sample agitation, leaching temperature, number of extractions, and storage prior to analysis, would then be systematically tested with each soil. Table 35 lists the variables to be tested in this study. One variable at a time will be changed, leaving all other variables constant. In this manner, all soils will be tested to determine not only the effect of each variable on the subsequent analysis, but also if there is any cumulative effect of two or more variables, such as the dramatic increase in ion concentration when increased water to soil leaching ratio was combined with the sample agitation by shaking seen in the preliminary study (Figure 52). From this study the combination of sample preparation variables will be determined which will leach as close to 100% of all ions from the soil for subsequent analysis. Thus when analyzed the result will match as closely as possible the true soluble ion content in the soil. This method can then be used as a standardized method of soil analysis for soils from extreme environments.

Due to the diversity in the soluble ion content in soils from different extreme environments, this study may find there is not one method of sample prepa-

Table 35: List of soil preparation variables to be explored in an in-depth study of the effect of soil preparation variables on the analysis of soils from extreme environments

| Separation Method | Leaching Solution | Leaching Ratio | Leaching Time | Method of Agitation | Leaching Temperature | Number of Extractions | Method of Storage |
|---------------------------|-------------------------------------|----------------|---------------|---------------------|----------------------|-----------------------|--------------------|
| Sieving Homogenization | 18.2 mΩ H ₂ O 1 M HCl | 1:1 | 10 min. | None | 5 °C | 1 | Benchtop Fridge |
| | | 5:1 | 1 hour | Shake | 25 °C | 2 | |
| | | 100:1 | 24 hours | Stir | 40 °C | 3 | |
| | | 250:1 | 48 hours | Sonicate | 80 °C | 5 | |
| | | 500:1 | | | | 10 | |

ration that works best for all extreme environment soils. Instead, it may be found that a different standardized method may be necessary for each extreme environment. Therefore, it may be necessary to complete an additional study, analyzing more samples from each environment to determine a standardized method of soil sample preparation for each extreme environment.

6 Novel Electrochemical TOC Analyzer for the Detection of Organics on Mars

6.1 Introduction

An overlying theme of the Mars Exploration Program is to determine if Mars is, or ever was, a habitable planet. Life as we know it on Earth requires water. Therefore, the strategy for the recent set of Mars missions, including the Phoenix mission, was to “follow the water,” to investigate the history of water on the planet. Instruments aboard the Phoenix Mars Scout Lander detected minerals such as CaCO_3 and other salts in the Martian soil in concentrations as high as several weight percent. The formation of these minerals requires water thus indicating the likelihood of the presence of water on the planet in the past. Likewise, a shallow ice table at depths of 5 to 18 cm was uncovered by the Lander’s robotic arm thus verifying the presence of H_2O on Mars. [106]

The presence of H_2O , even aqueous H_2O , does not necessarily mean the presence of life. Another requirement for life on Earth is organic materials. Therefore, the logical next strategy for future Mars missions would be “follow the organics,” to investigate the soils for the presence of organic materials. However, the discovery of organics on Mars would not necessarily imply a biological source, as it is possible that infall or abiotic pathways can account for many carbon-containing compounds.

Viking 1 and 2, the first missions to successfully land and operate on the surface of Mars, performed analyses of the Martian soil for the presence on organics, producing a seemingly negative result. Since that time, other missions, the 1999 Mars Polar Lander and the 2003 Beagle 2 Lander, carried instruments for organic detection to Mars, unfortunately neither mission was successful. [107, 108] Thus, the detection of organic material on Mars has

proven to be a difficult task.

This chapter will provide a background of the 1976 Viking organics data and the re-examination of these results over 35 years later along with the other organic detection instruments designed for current and future planned Mars missions. A different approach to organics detection on Mars through the analysis of total organic carbon (TOC) will be described along with the limitation of commercially available TOC analyzer for use on Mars. A discussion of the Mars Organic Carbon Analyzer (MOCA), a novel TOC analyzer designed specifically for the *in-situ* analysis of organics on Mars is presented followed by the initial experimental analysis performed on MOCA and the problems encountered. This chapter will conclude with a discussion of the development of MOCA as it stands to date and the future work necessary to produce a fully functioning technology readiness level 6 instrument.

6.1.1 Previous Mars Missions for Detection of Organics

The Viking Missions: The search for the presence of life on Mars began back in 1976 when the Viking Landers performed a set of experiments searching for the presence of organic material in the Martian soil. Viking 1 and 2 were both equipped with a thermal volatilization (TV)-gas chromatography(GC)-mass spectrometer(MS). The TV-GC-MS was designed to rapidly heat soils to temperatures of 200°C, 350°C and 500°C to break down large organic molecules into smaller organic molecules and to vaporize smaller organics molecules, then send the resulting fragments to be separated (via GC) and analyzed (via MS). The detection limits of this instrument were on the parts per million (mg/kg) range for some small molecules and the parts-per-billion ($\mu\text{g}/\text{kg}$) range for molecules containing two or more carbon atoms.

Results from these Viking experiments revealed no organics were present in

the soil at these detection limits and resulted in a strong argument against the presence of life on Mars. [109] This result was very surprising because even if there were no organics on Mars from either biotic or abiotic processes, organics should still have been detected from the average 2.4×10^8 grams of organic material which bombards the surface of the planet by meteoritic infall each year. [110] In fact, it has been calculated the surface of Mars should contain 0.0036 grams of carbon per gram of soil (or 3650 mg/kg organic carbon). [111]

Re-interpretation of the Viking Results: There has been much speculation as to the reasoning behind the Vikings negative results. One hypothesis for the negative Viking results is the oxidation of organics to non-volatile salts or carbon dioxide at the surface by the presence of oxidants and/or by direct UV irradiation. Due to the planet's low oxygen concentration in the atmosphere (0.13%) and the scarcity of liquid water, it has been suggested that the soil on Mars contains one or more potential oxidizers which could interact with the UV radiation to destroy organics on the surface. For many years it was believed peroxide was present in the Martian soil as the potential oxidizer. However, H_2O_2 is photolytically unstable in the Martian atmosphere and was found to be in concentrations too low to explain the Viking results. [112] The most recent in the long list of potential oxidizers is perchlorate which is used on Earth in solid rocket fuel. [58] Perchlorate was found in the northern polar region of Mars at a concentration of 0.6 wt.% by Phoenix. [19]

Since a potential oxidant presumed responsible for organic oxidation has yet to be confirmed, some generic pathways for the oxidation of organic molecules on Mars have been inferred. The starting organic materials used to infer these pathways were taken from known organics found in Martian meteorites (alkanes, alkylbenzenes, naphthalene, higher PAHs, kerogen, amino acids, and

hydroxyacids), thus avoiding the assumption the organics actually came from Mars. It was determined that the expected end products formed during oxidative destruction of these organics on Mars would not be CO₂ but rather aliphatic carboxylic acids (such as formic and oxalic acids) and/or aromatic carboxylic acids (such as benzoic and mellitic acids). These compounds are refractory organics (non-volatile and thermally stable). Since Viking was only capable of heating samples to 500°C, these compounds would not be detected. [113]

To test the hypothesis that the lack of organic detection by Viking was the limitation of the thermal volatilization step of the analysis, experiments were performed to detect organics in Mars analog soils by TV-GC-MS at higher temperatures. The analog soils included samples from the Antarctic Dry Valleys (near the junction of Victoria and McKelvey valleys) [114], and the Atacama Desert (near the Yungay area) [115], which have conditions similar to Mars due to their low biological and organic content. Also tested were soils from the Libyan Desert in Egypt (part of the Sahara), the Mojave Desert (in the southwestern United States), Rio Tinto (in Spain) and the Panoche Valley (in California). Samples were tested at 500°C, the upper limits of the Viking experiments, as well as 750°C. The total organic matter ranged from 10 to 1500 $\mu\text{g C}$ per gram of soil, with the soils from the Dry Valleys of Antarctica and the Atacama containing only 20 to 90 $\mu\text{g C}$ per gram soil as tested with conventional methods. When tested by the TV-GC-MS, no organics were detected in the ADV soils at either 500°C or the higher 750°C. However, none of the Atacama soils (near the Yungay area) had organics detectable by the TV-GC-MS when set at 500°C, but they were detectable at the higher 750°C. From this study it was determined that it is feasible that organics may be present on Mars but were not detected by the Viking's TV-GC-MS because they could

not be volatilized at the temperatures used and had higher temperature been achieved these compounds may have been detected. [109]

Recently a study was performed on Mars analog soils from the Atacama mixed with 1% magnesium perchlorate. This soil mixture was analyzed with the TV-GC-MS using the Viking heating protocol with an extended temperature range up to 1000 °C. The addition of 1% perchlorate was to more closely simulate what is known to be present in the Martian soil and determine how the presence of perchlorate in the soil may have affected the Viking results. Results from this study suggest a reinterpretation of the Viking results, that Landing Site 1 contained 1.5-6.5 mg/kg organic carbon and Landing Site 2 contained 0.7 to 2.6 mg/kg organic carbon in the presence of $\leq 0.1\%$ perchlorate. [84] There has been some criticism to this study. It has been stated that the proper blanks and background were not run in this analysis. Without the proper blanks and background it is possible to misinterpret the results from the experimentations performed. Therefore, even after 35 years the the findings and interpretation of the Viking missions' hunt for organics on Mars is still up for debate.

Phoenix's Thermal and Evolved Gas Analyzer (TEGA): As discussed in Chapter 1, one of NASAs goals for the Phoenix mission was to assess the habitability of the planet. The instrument aboard Phoenix charged with addressing the question of "life on Mars" (*i.e.*, the instrument that could detect organic material), was the Thermal and Evolved Gas Analyzer (TEGA). The TEGA aboard the Phoenix Lander was a modified version of the instrument which was aboard the ill-fated 1999 Mars Polar Lander. [116] The Phoenix version of TEGA consisted of a thermal analyzer (TA), a scanning calorimeter with eight high temperature ovens, an evolved gas analyzer (EGA), and a

magnetic sector mass spectrometer. A soil or ice sample was delivered to an oven where it was heated slowly at a constant rate from ambient to 1000°C. The evolved gases then traveled to a mass spectrometer sensitive to detection levels down to 10 parts per billion. At these concentrations it would be possible to detect trace amounts of organics present in the soil or ice. [117] Results from TEGA indicated there was a high temperature release of CO₂ beginning at 735°C identified as calcium carbonate (CaCO₃) and a lower temperature release of CO₂ starting around 400°C attributed to other forms of carbonate. However, TEGA did not show the presence of organics in the Martian soil analyzed. [27]

6.1.2 Upcoming Mars Missions for the Detection of Organics

Since the Viking missions of the 1970s there have been no other successful Mars missions containing instruments for the detection of organic material until the Phoenix Mars Scout Lander mission of 2007. However, there are plans for future Mars missions to contain different types of instrumentation for the detection of organics. The organic detection instruments designed for the Mars Science Laboratory (MSL) scheduled for launch in Fall 2011 and the European Space Agency's ExoMars mission currently scheduled for 2018 are discussed below.

MSL's Sample Analysis at Mars (SAM): The next scheduled Mars mission is the 2011 Mars Science Laboratory (MSL). The rover, named Curiosity, is equipped with an instrument suite designated Sample Analysis at Mars (SAM) focusing on the detection of organics, volatiles and light isotopes from samples collected with a robotic arm that can extend 1.9 meters. This instrument was designed to take up 63% of the scientific payload aboard MSL

emphasizing the importance of organics detection to this mission. [118] Members of the SAM instrument team have outlined the following scientific objectives: “(1) to take inventory of carbon compounds including those relevant to terrestrial life to determine their sources and processing, (2) to determine the chemical state of light elements through analysis of volatiles from minerals that trace aqueous and geological processes, (3) to examine oxidation chemistries that might play a role in the destruction of organic compounds and (4) to establish isotope ratios in noble gases and light elements that may constrain models of atmospheric evolution and past habitability conditions.” [119]

SAM consists of a suite of three instruments: a gas chromatograph (GC), a quadrupole mass spectrometer (QMS) and a tunable laser spectrometer (TLS). The GC-QMS is designed to separate and analyze soil samples for organic compounds, while the TLS is designed to detect methane, water vapor and carbon dioxide and determine the isotopic ratios of $^{13}\text{C}/^{12}\text{C}$ in methane and CO_2 and $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ in CO_2 . [120] The determination of isotopic fractionation is a good indicator of life as it is known on Earth. On Earth organic molecules tend to be deficient in the heavier ^{13}C isotope, favoring the lighter ^{12}C (*i.e.*, biological carbon sources will have a different $^{13}\text{C}/^{12}\text{C}$ ratio than abiotic carbon sources). Having an instrument capable of detecting carbon isotopes will allow for a better understanding of whether the organics detected come from biological or non-biological sources. [118]

Three different protocols have been established for the measurement of potential carbon compounds: (1) pyrolysis of soil samples followed by GC-MS and TLS analysis, (2) solvent extraction and derivatization of organics followed by GC-MS and TLS, and (3) combustion followed by TLS analysis of the CO_2 produced. The primary method is very similar to the analysis performed by Viking 1 and 2, however, the sample is heated to a much higher temperature

(1100°C) prior to GC-MS analysis, with these higher temperatures allowing for further pyrolysis of refractory organics. The second method used a derivatization agent to perform a single step derivatization on non-volatile compounds for detection via GC-MS. This method allowed for the detection of some non-volatile compounds, such as carboxylic acids, which could not be detected with the Viking instrumentation. The third method allowed for the combustion of kerogen-like organic material that would otherwise be difficult to detect via the other two methods. [120]

The SAM instrument has been tested in the laboratory using a variety of Mars analog samples including samples from the Atacama Desert. The instrument's pyrolysis was able to detect only benzene and formic acid in these samples. However, using the instrument's solvent extraction and derivatization method SAM was also able to detect trace levels of alanine, glycine, valine, proline, oxalic acid, benzoic acid, and acetic acid. Additionally, this instrument tested soils *in situ* as part of the 2006 Arctic Mars Analogue Svalbard Expedition (AMASE 06). Samples tested included a dolomite cemented deposit which was found to be rich in organic molecules, including a wide variety of linear and heterocyclic hydrocarbons. [120] The extensive testing of the SAM with analog soils and the positive result in the detection of a wide variety of organic compounds makes this instrument very promising in its ability to detect any organics which may be present on Mars. After 35 years, from Viking's first attempt to identify and measure the organic content on Mars, SAM may finally give the world the answer.

ExoMar's Two Possible Organic Detection Instruments: The European Space Agency (ESA) also has an upcoming mission tentatively set for the year 2018. The ESA's Exobiology on Mars (ExoMars) mission, like MSL,

is focused on the detection of biomarkers to determine whether or not there is or ever was life on Mars. The payload on ExoMars was originally scheduled to contain two instruments for organics detection: the Mars Organic Molecule (or Mass) Analyzer (MOMA) and the Mars Organic and Oxidant Detector (called the Urey). Since that time, the Urey has been scrapped from the upcoming ExoMars mission. However, the concept behind this instrument for the detection of organics on Mars will still be discussed.

Mars Organic Molecule Analyzer (MOMA): As with the SAM instrument aboard MSL, the Mars Organic Molecule Analyzer or Mars Organic Mass Analyzer (MOMA) is the largest instrument scheduled to be aboard the 2018 ExoMars rover. The main objective of this instrument is two-fold: 1) to detect the presence of organic materials, even at low concentrations, collected by drilling into the top 10 cm of Martian soil and 2) determine the chirality of the organic materials present to establish whether the organics are of biotic or abiotic origin. MOMA is designed to operate in two modes: gas chromatograph-mass spectrometer (GC-MS) mode and laser desorption-mass spectrometer (LD-MS) mode. [121]

In GC-MS mode, MOMA is very similar to Viking or SAM where soil samples are placed in an oven and heated to 900 °C, thus evaporating all volatile components. The volatiles are then measured via GC-MS. [121] The one difference is the type of mass spectrometer used. Viking and SAM were designed to use a magnetic sector MS, which has a limited mass range with a maximum mass of 215 Da on Viking and 535 Da on SAM. [122] The MS aboard MOMA is a low power quadrupole ion trap mass spectrometer capable of a mass range up to 2000 Da. [123] Another unique feature to MOMA is some of the ovens are designed to contain a derivatisation agent making the

some samples suitable for chiral analysis. [124]

In LD-MS mode, a laser desorption ion source capable of evaporating non-volatile organic molecules is used to ionize a small area of the soil sample. The ions are then measured by the ion trap MS. [121] This mode can be used for the determination of less volatile organics as well as for heat-resistant material which would be difficult if not impossible to analyze in GC-MS mode. [124]

Testing of various components of MOMA began in 2009 at both the Max Planck Institute for Solar System Research (MPS) and the Johns Hopkins University School of Medicine (JHU SoM). [124] In 2010, field tests were performed using a breadboard model as part of the Arctic Mars Analog Svalbard Expedition 2010 (AMASE). The oven, trapping station and gas chromatograph were tested on site. However, the breadboard did not include the mass spectrometer. [125] Much more testing needs to be performed on the MOMA including a performance test of the complete system coupling both the gas chromatograph as well as the laser desorption system to the mass spectrometer. [123, 124]

Mars Organic Detector (MOD): The other organic detection instrument designed for the ExoMars mission was dubbed Urey in recognition of the notable chemist Harold Clayton Urey. Also known as the Mars Organic and Oxidant Detector, the focus of Urey is two-fold. The first focus is to detect organic molecules on Mars, specifically amino group compounds (such as amino acids, amines, nucleobases and amino sugars) and polycyclic aromatic hydrocarbons (PAHs). The second focus is to investigate the oxidation state of the Martian soil via the Mars Oxidation Instrument (MOI) to determine what oxidative processes on Mars are responsible for the destruction of organics at the planet's surface. [126]

The instrument for the detection of organics, the Mars Organic Detector

(MOD) or Mars Organic Analyzer (MOA), consists of a sub-critical water extractor (SCWE), laser-induced fluorescence (LIF) and micro-capillary electrophoresis (μ CE). The SCWE is designed to leach organic material from soil and rocks. The organics are subsequently sublimated and then sent to the LIF for detection. LIF is capable of detecting PAHs because they fluoresce naturally. However, organic amines do not and therefore must be combined with fluorescamine in order to be detected. LIF is 10^4 times more sensitive a technique than the GC-MS technique used by Viking. The detection limits are in the parts-per-trillion range. If amino acids are found by LIF, the sample can then be sent to the micro-capillary electrophoresis to determine their chirality. The μ CE is another extremely sensitive instrumental technique with detection in the parts-per-trillion range. [126] On Earth life has evolved to favor “left handed” molecules, or l-amino acids. Likewise, amino acids found in organic-containing meteorites have also been found to be “left handed”. As with isotopic fractionation, chirality can also be used to determine if organics come from abiotic or biological sources. [119]

As with the other Mars instruments for life detection, the MOD, in particular the micro-capillary electrophoresis, was tested with samples from the Yungay region of the Atacama Desert. Concentrations ranging from 50 to 100 μ g/kg amines and amino acids were observed. [127] The results were compared to analysis performed by traditional HPLC amino acid analysis and found to be highly consistent. Other samples from the Panoche Valley in California were also analyzed with detection from 70 parts per trillion to 100 μ g/kg amino acids, thus confirming the parts per trillion sensitivity of this instrument. [83] Despite all the hype received over this instrument back in 2008, the Urey is no longer scheduled to be a part of the 2018 ExoMars mission.

6.1.3 A Different Approach - Total Organic Carbon Analysis

The two previous Mars missions, Viking and Phoenix, as well as the two scheduled missions, MSL and ExoMars, were all equipped with similar methods for the detection of organics on Mars (Table 36). [122] The four instruments all use pyrolysis to volatilize organics followed by electron impact ionization and analysis by a mass spectrometer, with slight variations. The advantage of using a mass spectrometer allows for any organic present to not only be detected but also to be individually identified.

However, a quicker way to simply determine the presence or absence of organics on Mars would be through the use of a total organic carbon (TOC) analyzer. Therefore, it has been proposed a TOC analyzer should be tested as a different approach to the detection of Martian organics. A description of TOC and the presence of TOC in extreme environments on Earth is discussed below. This is followed by a discussion of the types of TOC instruments currently available and the detectors used along with the limitations of these commercial TOC instruments for the detection of TOC on Mars.

What is Total Organic Carbon?: Total carbon (TC) is the sum of both the total inorganic carbon (TIC) and the total organic carbon (TOC) constituents in a sample. Types of inorganic carbon include: carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). [128] All these species are related by the following pH driven chemical equilibria (Equation 13).



Table 36: Comparison of analysis techniques for the detection of organics on past and future Mars missions. [122]

| Year | Mission | Instrument | Volatilization | Ionization | Analyzer | MS Mode | Max Mass (Da) |
|------|---------|------------|--------------------|------------|----------|--------------------|---------------|
| 1976 | Viking | GC-MS | Pyr (500°C) | EI | sector | GC-MS | 215 |
| 2007 | Phoenix | TEGA | Pyr (1000°C) | EI | sector | Pyr-MS | 140 |
| 2011 | MSL | SAM | Pyr (1100°C) | EI | QMS | Pyr/GC-MS | 535 |
| 2018 | ExoMars | MOMA | LD Pyr (1000°C) | LDI EI | ITMS | LD-MS Pyr/GC-MS | 2000 |

Total organic carbon (TOC) refers to all carbon bound in organic molecules. TOC can be defined further as either purgeable organic carbon, also known as volatile organic carbon (VOC), or non-purgeable organic carbon (NPOC). VOC is carbon that can be removed from a neutral or acidified solution via purging with an inert gas. In contrast, NPOC cannot be removed by purging. [129]

The amount of TOC in a sample can be measured in one of two ways: indirect or direct. In the indirect method, the TC is measured along with the IC and the difference is the TOC (Equation 14):

$$\text{TOC} = \text{TC} - \text{IC} \quad (14)$$

The TOC measured is both the VOC and the NPOC. In the direct method, the TOC is measured after the removal of the IC. In this method, the sample is typically acidified to drive the chemical equilibria towards $\text{CO}_{2(g)}$ and then purged with an inert gas to remove the IC in the form of gaseous CO_2 . However, VOC is also removed, and thus the TOC measured is actually the total NPOC. [129]

Applications of TOC Analysis: The measurement of TOC is vitally important due to its impact on human health, manufacturing processes and the environment. There are several different fields that use TOC analyzers on Earth, the biggest being the detection of contaminants in drinking water. Prior to purifying drinking water, there are many organic contaminants from both natural (*i.e.*, humic acid, urea, etc.) and synthetic (*i.e.*, detergents, fertilizers, pesticides, etc.) sources. TOC analyzers are used to determine the amounts of contaminants pre- and post treatment. [130]

Another use for TOC analysis is in the pharmaceutical industry for cleaning

verification. TOC analyzers are used to ensure cleaning procedures are working properly and adhering to the proper standards to prevent cross contamination. TOC analysis is replacing HPLC analysis and spectrophotometric analysis in this field due to its faster analysis time. [131] Oil exploration also uses TOC analysis because it allows for the analysis of source rocks, which are rocks that contain or could produce hydrocarbons. [132]

TOC analysis is not limited to uses on Earth. The international space station (ISS) uses a TOC analyzer called the Total Organic Carbon Analyzer, or TOCA, to examine the stored and re-claimed water supply and assess the quality of this water to determine if it is safe for human consumption. The first generation TOCA required the addition of small quantities of hazardous chemicals to monitor the water quality. [133] However, a second generation TOCA had been recently developed which does not require the use of any hazardous reagents. [134]

TOC in Extreme Environments: With currently available instrumentation it is possible to determine the total organic carbon (TOC) in soils anywhere on Earth. In fact, measurements of TOC have been performed even in the Earth's most extreme environments such as the Atacama Desert in Chile and the McMurdo Dry Valleys in Antarctica. Globally, the TOC present in soil is known to decrease with the mean annual precipitation as a result of the balance of organic input (mostly from plants but a small portion from the atmosphere) and losses. [135]

The hottest place in North America, Death Valley, is located in the Mojave Desert (Eureka Valley, CA). The Mojave receives ~140 mm of rainfall a year [136] and has a measured TOC of 7,000 mg/kg [80]. The world's largest hot desert, the Sahara (Abu Simbel, Egypt), is even more arid receiving >10 mm

rain per year in its most arid center [137] and has a measured TOC of only 1,700 mg/kg [80]. Therefore, it is expected that in Earth's most hyperarid regions, the Atacama Desert and the Antarctic Dry Valleys, would contain very small amounts of TOC.

The Yungay region of the Atacama Desert, from 22°S to 26°S latitude (see Figure 33), is considered the driest part of the Atacama. Analysis of soils from this region with commercial TOC analyzers have detected TOC ranging from 200 to 765 mg/kg in surface and subsurface samples. In all cases, these measurements were above the limits of detection (LoD = 200 mg/kg) and below the limits of quantification (LoQ = 1,000 mg/kg) for the TOC instrumentation used. [79, 80, 138] It has also been found that the amount of TOC increases slightly with depth, though the concentration is still very low and variable. [135] This could indicate oxidation at the surface. Atacama is supposed to be highly oxidizing. Analysis of the soil in this region was also analyzed via subcritical water extraction, an instrument designed in part for the suite of instruments designated *Urey*, an organic and oxidant detector for the European Space Agency's ExoMars mission. This method detected 0.2 to 55.4 mg/kg TOC which are much lower concentrations than previously recorded for this area. [138]

Analysis of TOC from soil in the McMurdo Dry Valleys by commercial TOC analyzers have also been performed. The majority of published data for organics analysis in the MDV is focused on samples from Taylor Valley either in soils [139, 140, 141, 142, 143] or snow [144]. Organic analysis was also performed in soil samples from Wright Valley [145] and Garwood Valley [146, 143]. The reasoning behind focusing the study of organics around Taylor Valley was its ease of accessibility and relatively wetter environment with streams and lakes. [146] Garwood Valley is also one of the wetter valleys. [143]

In all studies from Taylor and Garwood Valleys the soil samples analyzed were near water sources, either ponds or lakes.

TOC values were published in two ways from these studies: either in concentration and/or in material density (mass per unit area). The carbon density in soils from Taylor Valley was reported an average of 257 g/m² with a high of approximately 1250 g/m². [140] In Garwood Valley the material density of carbon in soils was measured at a much higher 6000 ± 1900 g/m². [146] As for the concentration of TOC in these valleys, values of 0.23 to 0.37 μg/kg [141], up to 0.35 μg/kg [142], and 4 μg/kg [140] of TOC in Taylor Valley soils, and 108 to 264 μg/kg [144] of TOC in Taylor Valley snow have been reported. A higher concentration of TOC in soils was found in Garwood Valley, 0.27 to 60.09 μg/kg. [146] These concentrations are orders of magnitude lower than the concentration of TOC seen in the soils from the Atacama Desert. Recently, the TOC level in soils from the South Fork in Wright Valley near Don Juan Pond have been reported in the range of 58-806 mg/kg [145], much higher in concentration than any other location in the MDV and similar to the concentration seen in the Atacama's Yungay region.

To date there have been no published reports of TOC in the MDV in the stable upland zone. However, soils from Beacon Valley collected as part of the IPY (see Chapter 2) were recently analyzed for TOC. This analysis reported an upper limit of 500 mg/kg in the soil. While this upper limit is higher than the levels of TOC reported in the lower coastal thaw zone, it is orders of magnitude lower than the levels from South Fork in Wright Valley, Antarctica or the Atacama Desert.

Limitations of Current Commercial TOC Analyzers for use on Mars:

All TOC analyzers operate on the same basic principle. Water-soluble organic

material is converted to CO₂ which is subsequently detected. Since there is one mole of carbon per one mole of CO₂ produced, the moles of TOC are easily calculated. Most commercially available TOC analyzers are large, heavy, and require a lot of power. Although suitable for laboratory applications, this limits their viability for *in situ* analysis, especially in remote environments or for use on other planets. Additionally, commercially available TOC analyzers use either hazardous reagents, ultraviolet light and/or high temperature ovens to convert organics to CO₂ further adding to their limitations for *in situ* analysis. The currently used methods for TOC detection are outlined below.

Types of TOC Analyzers: Most commercially available TOC analyzers use one of two methods for the conversion of TOC to CO₂: combustion or UV/chemical oxidation. There are two types of combustion methods, high temperature combustion and high temperature catalytic combustion, both of which use high temperature ovens to convert organics to CO₂. In the high temperature combustion method, TOC is placed in a >1,000-1,100°C oven with an oxygen-rich environment where the carbon reacts with oxygen forming CO₂. In the high temperature catalytic combustion method, the temperature of the combustion oven is set at a lower temperature and uses a catalyst along with the oxygen-rich environment to oxidize the organics. Some common catalysts include Cr₂O₃, CoO and CuO which can be used at a temperature of 950°C or metals such as Al, Co, Cu, Ir, Ni, or Pt which can be used with an even lower temperature of 680°C. Whichever catalyst is chosen, the carbon reacts with oxygen producing CO₂, just like in the high temperature method. [128, 129]

In the UV/chemical oxidation methods, a combination of UV light and chemical radicals are used to oxidize the TOC. Photochemical oxidation using only UV light can be used to oxidize TOC to CO₂ but more often a

UV/chemical oxidation method is used where UV light is coupled with peroxodisulfate in solution. In this method, the UV light produces the following free radical oxidations (Equations 15, 16 and 17).



Likewise, the UV light also excites the organics, R, (Equation 18) and the excited organics react with the free radicals to produce CO₂ (Equation 19). [128, 129]



It is also possible to use heat in place of UV, called the peroxodisulfate/heat method, to produce the necessary radicals (SO₄^{-•} and OH[•]) for TOC oxidation. [147]

TOC Detection Methods: Since commercial TOC analyzers convert the organic material to CO₂, the detectors used in these instruments are simply CO₂ detectors. CO₂ can be measured in either the aqueous or gas phase. First, two common detectors used in commercial TOC analyzers, one gas phase and one aqueous phase, are discussed. Then two alternative detectors, again one gas phase and one aqueous phase, are presented.

Conductivity: Conductivity cell detectors are used when the CO₂ produced is in the aqueous phase. Conductivity cell detectors can be further

divided into two categories: direct conductivity and membrane conductivity. The conductivity of the dissolved CO_2 in solution is measured directly with a direct conductivity cell; while in a membrane conductivity, the dissolved CO_2 must first pass through a hydrophobic gas permeation membrane prior to measuring the conductivity. Using the membrane conductivity cell improves the accuracy of the measurement compared to the direct conductivity measurement. In both types of detectors the conductivity of the solution is measured before and after organic carbon oxidation. The difference in the conductivity, caused by the dissolved CO_2 from the oxidized organic carbon forming a weak acid in solution, is proportional to the concentration of TOC in the original sample. [128]

Non-dispersive Infrared (NDIR) Sensor: NDIR detectors are used when the CO_2 produced is in the gaseous phase. NDIR detectors use a single path, dual wavelength, infrared detection system where the CO_2 measurement is a function of the absorption of IR energy. The sample chamber has an optical filter centered around $4.24 \mu\text{m}$, which corresponds to the absorption band for CO_2 . A second reference chamber has an optical filter centered around $3.95 \mu\text{m}$, which experiences no absorption from CO_2 and will receive the full energy of the source. The ratio of the two is the amount of light absorbed by the CO_2 , which in turn is the concentration of CO_2 produced by the oxidation of organic carbon and thus proportional to the TOC in the sample. [148]

NDIR spectrometry is a popular detection method for TOC analysis because in addition to being inexpensive and durable, this method provide a high sensitivity and low detection limits. [128, 129] Additionally, NDIR spectrometers with a third optical filter centered around the absorption band for $^{13}\text{CO}_2$ are also available which can measure the isotopic ratios of $^{12}\text{CO}_2$ to $^{13}\text{CO}_2$.

Therefore, NDIR spectroscopy can be used to measure not only total carbon but also carbon isotopic ratios. [149]

CO₂ Ion Selective Electrode: An alternative detector of CO₂ in the aqueous phase is a CO₂ ion selective electrode (ISE). A CO₂ ISE is a type of gas sensing ISE which uses a gas permeable membrane to separate the solution of interest from the inner filling solution. As dissolved CO₂ permeates the membrane, the partial pressure of CO₂ inside and outside the ISE begins to equilibrate. When equilibrium is reached, the partial pressure of CO₂ is proportional to the concentration of CO₂ in the sample. Once the concentration of CO₂ is known it is possible to determine the TOC of the sample. Common interferences to CO₂ sensors include: formic acid, acetic acid, sulfur dioxide, nitrogen dioxide, and water vapor. [150] These known interferences are a drawback to this method of detection.

Residual Gas Analyzer: An alternative detector for CO₂ in the gas phase is a residual gas analyzer (RGA). An RGA is a type of small mass spectrometer with a mass range of one to a few hundred atomic mass units, making it suitable for the detection of small molecular weight gases such as CO₂. As with any mass spectrometer, molecules of gas are ionized and separated by mass. For TOC detection, the RGA can be set to monitor m/z 44 (the molecular weight of CO₂) and m/z 45 (the molecular weight of ¹³CO₂) allowing for simultaneous detection of both carbon isotopes (¹²C and ¹³CO₂). The RGA can also simultaneously measure other gases, such as H₂ (m/z 2), O₂ (m/z 32), and water vapor (m/z 18), which are also produced during the oxidation process. The drawback to this detector is its size, mass, and power requirements.

6.1.4 Mars Organic Carbon Analyzer (MOCA)

To overcome the limitations of commercially available TOC analyzers previously discussed, a new type of *in situ* TOC analyzer has been proposed as a means of detecting and quantifying organics in Martian soils. Unlike commercially available systems which use either high temperatures, UV or harsh chemicals to oxidize organics to CO₂, this new instrument uses an electrochemical approach to oxidation. The instrument known originally as TIC-TOC (short for **T**otal **I**norganic **C**arbon-**T**otal **O**rganic **C**arbon) consisted of both a chemical oxidation system (for analysis of both inorganic and organic carbon) and an electrochemical oxidation system (for analysis of organics which were found hard to oxidize chemically. [151] However, the instrument then evolved into a fully electrochemical system re-named the Mars Organic Carbon Analyzer (MOCA). [152] Removal of the chemical oxidation system considerably decreased the size and complexity of MOCA.

The MOCA instrument consists of two main components: an electrochemical oxidation cell and a detector. The detector can be any system capable of CO₂. Detectors used to date include a residual gas analyzer and a non-dispersive infrared (NDIR) gas analyzer. Due to the wide variety of detectors capable of being used in this instrument the focus of the instrumental development was centered around the electrochemical cell, the working electrode material and the corresponding mechanism(s) of oxidation.

Electrochemical Cell Designs: The electrochemical cell consists of several parts: a housing for the working and counter electrodes, a solution reservoir, a stirring mechanism, a power supply and in one configuration, a pump. The MOCA has undergone three different electrochemical cell configurations to date. The main limitation to the electrochemical cell design has been the size

and shape of the working electrode.

MOCA Version 1: The original working electrode was a solid circular disk boron-doped diamond (BDD) electrode measuring 2.5 cm in diameter and 2 mm in thickness (for a total surface area of 11.3 cm²) with a 1.2 cm “connector” for attachment to additional wiring or an alligator clip (Figure 54). Due to the large size of the working electrode, the first electrochemical cell configuration (Version 1) consisted of a 250 mL three neck round bottom to serve as both the housing for the electrodes and the solution reservoir (Figure 54). The large size flask was necessary to allow the working electrode and Pt counter electrode (of similar size but smaller thickness) to fit through the middle neck and suspend into solution inside the middle of the flask. A stir bar placed at the bottom of the flask with the flask was used as a stirring mechanism when placed on a stir plate, and the electrodes were connected by wire through a rubber stopper placed in the middle neck of the round bottom flask to an off-the-shelf power supply (an EG&G Model 263A Potentiostat). Two stopcock adapters were connected to the other two necks of the flask, one for purging the solution reservoir prior to analysis and the other for connection of the electrochemical cell to a suitable detector. The main drawback to this method was the large solution reservoir. In order for the electrodes to be fully submersed into solution the sample volume needed to be at least 200 mL.

MOCA Version 2: To overcome the need for such a large sample volume a second scaled down version of the original electrochemical cell was fabricated (Version 2). This version used the same concepts outlined above but with a smaller 15 mL round bottom flask. The working electrode designed to fit into this scaled down cell was rectangular in shape measuring 1.1 cm by 2 cm and 2 mm thick (for a total surface area of 5.6 cm²) with a 1.2 cm “connector”



Figure 54: Original boron-doped diamond working electrode (on top) for the use in MOCA Version 1 (on bottom) The detector and power supply are not shown.

for attachment to additional wiring or an alligator clip (Figure 55). The the working electrode was BDD coated on a niobium substrate and manufactured by Condias Conductive Diamond Products (Itzehoe, Germany). This modification of the electrochemical cell design allowed for the sample solution volume to be reduced from 200 mL to 10 mL, a much more reasonable volume. However, this design also had some major drawbacks. Like the original design, the working and counter electrodes were dangled inside the flask making it difficult to keep a consistent electrode spacing of 1 cm. However, the biggest drawback to this design was the inability to achieve a sealed system with no gas leakage. With the decreased solution reservoir there was also reduced headspace for the oxidized CO₂ gas to collect. The pressure increased rapidly inside the reservoir causing the cell to leak at one or both of the stopcock adapters.

MOCA Version 3: The third and latest electrochemical cell design (Version 3) is a drastically different design from Versions 1 and 2.. This design is a flow-through system in which the electrode housing is separate from the solution reservoir. Separation of the electrodes from the solution reservoir allows for several advantages. The size of the electrode housing can be fixed to the exact specifications of the electrodes and allow for consistent electrode spacing of 1 cm apart (Figure 56). The working electrode designed for this version of MOCA is BDD coated on tungsten wire manufactured by the Diamond Lab, Department of Chemical Engineering at Case Western Reserve University. The BDD-coated wires measure 4.2 cm long with a diameter of 0.5 mm for a total surface area of 0.66 cm².

As with the electrochemical cell, the solution reservoir size does not depend on the size of the electrodes and with the use of a small pump the system becomes inherently self-stirring. In this design, the solution is pumped from

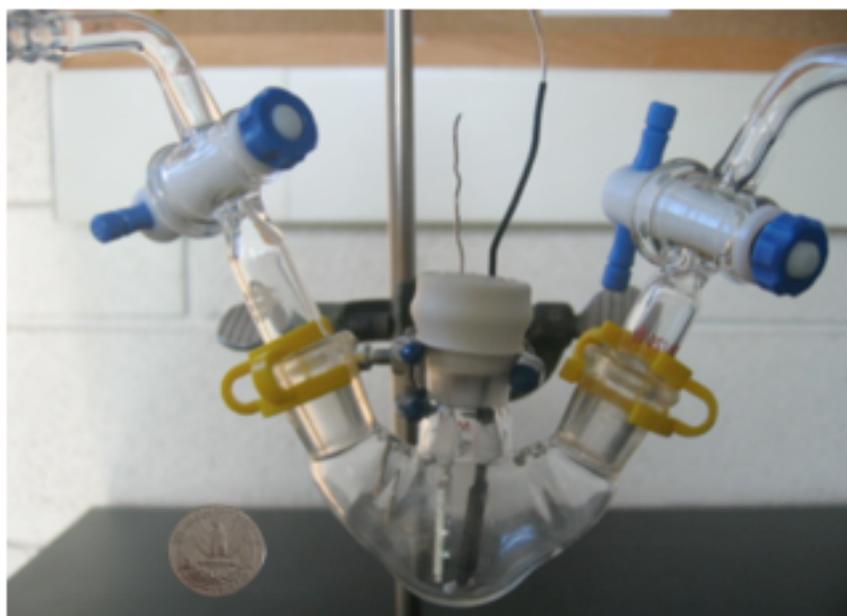


Figure 55: Modified boron-doped diamond working electrode (on top) for use in MOCA Version 2 (on bottom) The detector and power supply are not shown.

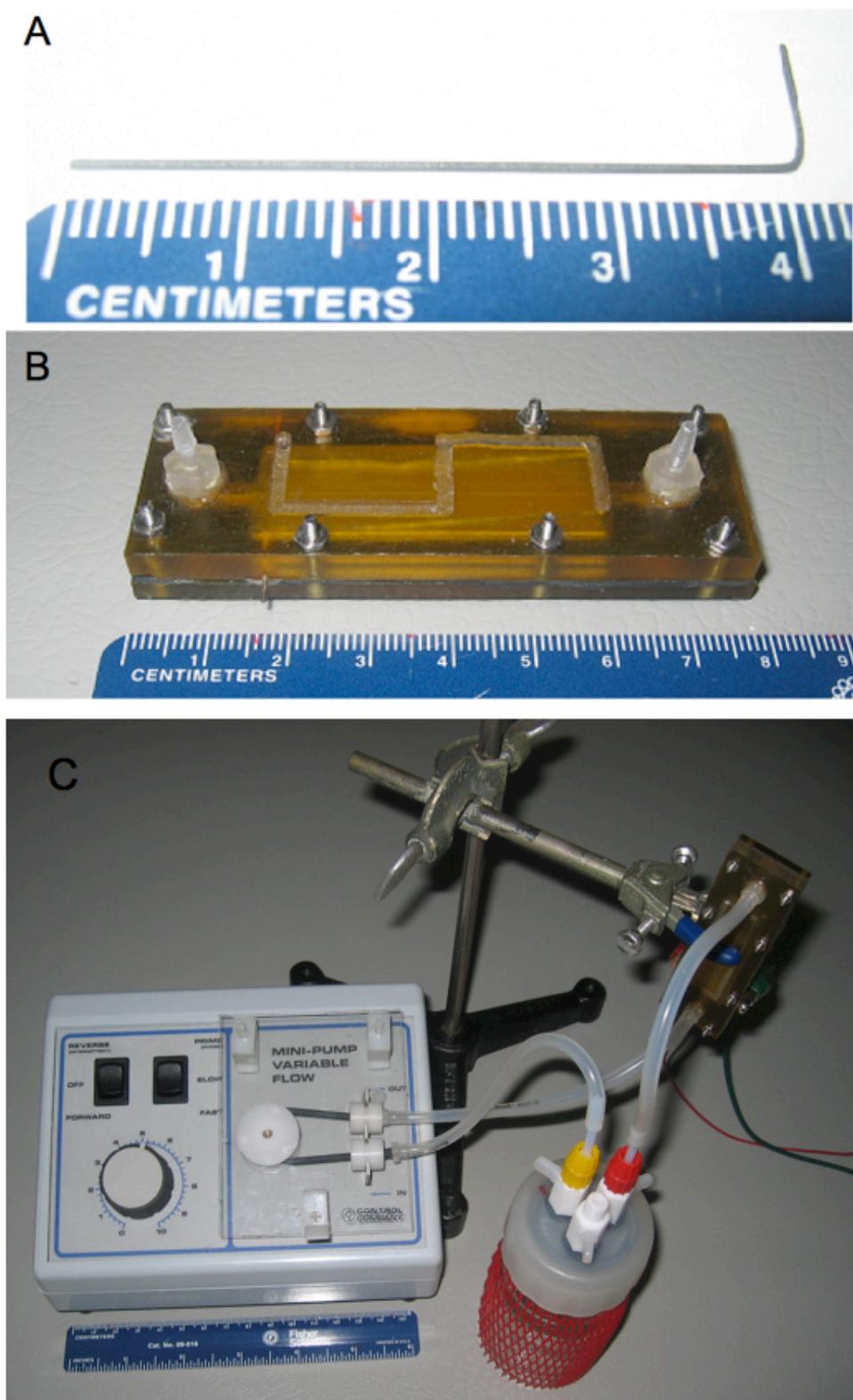


Figure 56: (A) BDD coated W-wire anode and (B) Electrochemical flow-through cell for use in (C) MOCA Version 3. The detector and power supply are not shown.

a 100 mL reservoir with Omnifit top (Ace Glass) by a peristaltic or gear pump to an poly[ethyleneimine] (PEI) electrode housing were the electrodes are connected via alligator clips to a commercial power supply (an EG&G Model 263A Potentiostat) and then back into the reservoir. Attached to the top of the solution reservoir is a stopcock to allow for purging prior to oxidation and connection to a suitable detector (Figure 56).

In its current state of design the MOCA Version 3 is at a NASA technology readiness level (TRL) 4. A TRL 4 means that a prototype of the instrument has been built and tested in the laboratory. [153] The current design of the electrochemical cell and solution reservoir weighs less than 7.5 kg and requires less than 2 W of power. Coupled with a non-dispersive infrared (NDIR) gas analyzer, the entire MOCA weights less than 9.5 kg and requires less than 16 W of power. This is already substantially smaller, lighter and requires much less power than any commercially available TOC systems.

Electrodes: There are a variety of different electrode materials available. These electrodes can be divided into two categories: Class 1 and Class 2. Class 1 electrodes, known as “active,” include carbon, graphite, iridium oxide (IrO_2), ruthenium oxide (RuO_2), and platinum. These electrodes have a low oxygen evolution overpotential which makes them good electrocatalysts for oxygen evolution (Equation 20) and a poor choice for the oxidation of organics permitting only partial oxidation. Class 2 electrodes, known as “non-active,” include antimony-doped tin oxide (Sb-doped SnO_2), lead oxide (PbO_2) and boron-doped diamond (BDD). These electrodes have a high oxygen evolution overpotential which makes them a poor electrocatalyst for oxygen evolution and a good choice for the oxidation of organics because they favor a complete oxidation to carbon dioxide. [154]

Carbon and graphite electrodes have the advantage of being made cheaply with a large surface area, but at high current densities these electrodes are prone to surface corrosion which causes electrode deactivation. Platinum electrodes are one of the most commonly used due to their good chemical resistivity to corrosion but as a Class 1 electrode they tend to provide a less than complete oxidation of organics. Likewise, the oxides of Ru, Ti and other metals, known collectively as dimensionally stable anodes (DSA), are also Class 1 and have the same tendency of providing a less than complete oxidation of organics. Antimony-doped tin oxide electrodes have a high oxygen overpotential of 1.9V versus SHE but are limited by a short service life. Lead dioxide electrodes have a good conductivity and a large overpotential for oxygen evolution in acidic media, however, in basic media there is the possibility for these electrodes to release toxic lead ions. [154]

The electrode of choice for MOCA is boron-doped diamond (BDD). There are many advantages to using BDD electrodes. BDD electrodes consist of an inert surface which results in low adsorption properties and a high resistivity to deactivation due to the electrogeneration of active hydroxyl radicals which can oxidize any polymeric material on the surface. They also are stable against corrosion even in applications requiring very acidic conditions. Additionally, BDD electrodes exhibit an extremely high oxygen evolution overpotential with a low and stable voltammetric and amperometric background current. [154, 155]

The disadvantage to BDD electrodes are their comparatively high cost versus other types of electrodes. This cost is due in part to the limited availability of these electrodes. As of 2004, there were four commercial suppliers of BDD electrodes: Fraunhofer USA (East Lansing, Michigan), Condias GmbH (Germany), Sumitomo Electric USA Inc. (Torrance, CA), and sp3 Diamond

Technologies (Santa Clara, CA). [156] Additionally, there have also been problems with finding an appropriate substrate on which to deposit the BDD layer. Additional information on BDD fabrication is discussed below.

BDD Electrode Substrates: Boron-doped diamond (BDD) electrodes are fabricated from the growth of a diamond thin film on a substrate material. They can be grown homoepitaxially, meaning on diamond itself, or heteroepitaxially on some other non-diamond material. [157] Possible choices for heteroepitaxial growth materials include: silicon (Si), tungsten (W), molybdenum (Mo), tantalum (Ta), titanium (Ti), nickel (Ni), and niobium (Nb). [157, 158, 159] These materials all possess a high melting point which can withstand the high temperatures encountered during the deposition process and are all capable of forming a carbide, a compound composed of carbon and a less electronegative element. The main difficulty with heteroepitaxial growth is getting the diamond to begin adhesion to the substrate material. Thus the formation of a carbide layer acts like a glue which can help to hold the diamond layer to the substrate material. [157]

The use of metals for the deposition of BDD is limited by their high cost as well as the ability of the substrate material to adhere strongly to the underlying substrate without the problem of delamination. Though the formation of a carbide layer is possible with all the substrate materials listed above, delamination is still possible. Large thermal residual stress can lead to delamination by causing the dissociation of the metal-carbon layer. [160] Silicon is the most commonly used substrate for BDD electrodes. Not only is silicon relatively cheap but it has a crystal structure similar to diamond allowing for localized carbide formation. [147] Silicon also has a low thermal expansion coefficient meaning that changes in temperature will not cause this material to expand

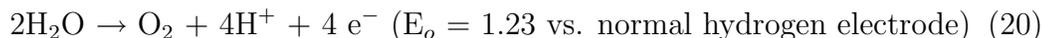
or contract breaking off the diamond coating. [157] The drawback to silicon has always been its brittleness meaning electrodes grown on this substrate are known to break easily. [154] Thus, there is no perfect substrate material for the deposition of diamond.

BDD Electrode Fabrication: The most common method for the growth of BDD electrodes is chemical vapor deposition (CVD). In the CVD process, a substrate material is exposed to one or more volatile precursors with which it reacts and produces the desired deposit on the substrate surface. There are two common methods of CVD: microwave plasma assisted (MPA) and hot filament (HF). In both methods, the substrate material is treated in a piranha solution (a 3:1 mixture of concentrated H_2SO_4 to 30% H_2O_2) to remove any organic contaminants from the surface. The substrate is subsequently seeded with diamond powder (0.1-10 nm particle size) typically though pre-abrasion of the surface by ultrasonic agitation before being placed into the deposition chamber. [161, 162, 163, 164, 165]

MPA-CVD and HF-CVD differ in the manner in which the process gas, typically 1-2% by volume methane in a background of hydrogen (with the addition of borane gas, B_2H_6 , which provides the B source for the boron-doped diamond) is activated, producing the diamond precursors that interact with the seeded substrate surface beginning diamond growth. MPA-CVD uses various forms of plasma, including DC, RF, microwave, electron cyclotron resonance microwave and high-pressure plasma, to produce the carbon precursors for diamond growth. In HF-CVD, the seeded substrate material is placed on top of a heater (between 700 and 1000 °C and at a pressure of 1-10 kPa) and approximately 2.5 cm below a coiled metal tungsten filament and uses the heated filament to produce the carbon precursors for diamond growth from the

process gas. Once the diamond precursors are produced in the gas phase, they interact with the seeded substrate surface and individual nucleation sites grow as individual grains expand in diameter until they eventually coalesce into a continuous film. [161, 162, 163, 164, 165] The MPA-CVD method is suitable for deposition of a small surface area because it is limited by the wavelength of the microwave radiation, while the HF-CVD method is most suitable for the depositions of large surface areas. Surface areas as large as 0.5 m² have been successfully coated via this method. [147]

Mechanisms of Oxidation: When using a BDD electrode for the oxidation of organics there are two possible mechanisms of oxidation: direct and indirect. In the direct oxidation mechanism an anodic peak is observed in the region below that of oxygen evolution in the region of water stability (Equation 20).



This oxidation reaction is direct in that it occurs without the presence of an electrogenerated intermediate. [147]

The indirect mechanism involves a two-step process. In the first step, a hydroxyl radical is generated via water discharge on the BDD surface (Equation 21).



In the second step, the hydroxyl radical is used to oxidize the organic; for example, formic acid (Equation 22), at the electrode surface.



The main side reaction of the indirect mechanism is the evolution of oxygen

(Equation 20). [147] In the case of both the direct and indirect mechanisms only organics that reach the electrode surface can be oxidized, therefore, mass transfer limits the reaction, especially at low concentrations of organics. This problem can only be overcome by increasing either the concentration of organics to be oxidized or the size of the anode.

6.2 Experimental

The following sections outline the experimental testing performed with MOCA. Before any testing was possible, a list of potential test compounds was established. Once the organics of interest were chosen testing began with cyclic voltammetry to determine the mechanism of oxidation for each of the organics to be studied. An overview of the oxidation procedure for all three versions of MOCA is then presented. Finally, more detailed procedures will be presented for a variety of different experimentations using MOCA Version 3 only.

Organics of Interest: Before any testing of MOCA could commence, it was necessary to determine a list of organics which would be suitable test compounds for the initial studies. MOCA is being designed for detection of organics on Mars, therefore, organics likely to be present on the surface of Mars are the top priority. Thus compounds were chosen from those listed as interstellar molecules or known to be present in Martian meteorites, because these organics are more likely to be found on the Martian surface. Also, the organics needed to be of low molecular weight, less than a few hundred grams per mole and containing less than ten carbon atoms. The assumption being any organics present on Mars have been at least partially broken down by some oxidative process, such as by the presence of oxidants in the soil and/or by direct UV irradiation, and therefore contain fewer carbons and are

smaller in size. In fact, it has been determined that oxidative destruction would lead to end products of aliphatic carboxylic acids (such as formic and oxalic acids), and/or aromatic carboxylic acids (such as benzoic and mellitic acids). [113] From these criteria, nine organics were chosen for the initial investigation. Table 37 lists the organics chosen then number of carbon atoms, their molecular weight, and the reason for their selection.

6.2.1 Cyclic Voltammetry

Cyclic voltammetry (CV) of each of the nine organics listed in Table 37 was performed using both polished glassy carbon (GC) and boron-doped diamond (BDD) working electrodes, Pt wire as the counter electrode and an Ag/AgCl reference electrode in the standard 3-electrode cell configuration. A blank solution of 0.1 M H₂SO₄ (the electrolyte solution only) was first run, followed by 25 mM of each organic in 0.1 M H₂SO₄ background electrolyte. CVs were run from -1V to 2V at a scan rate of 50 mA/sec with a sensitivity of 1 mA/V. The purpose of this study was to determine whether the mechanism of oxidation of each compound was direct or indirect.

6.2.2 Oxidation Procedures

The following experimental procedure is a generalized overview of a single MOCA Version 1 and 2 or MOCA Version 3 experiment. Specific parameters such as the electrolyte, organic, detector, and current used varied depending on the experiment being performed. However, the overall experimental process remained the same.

MOCA Versions 1 and 2: Analysis in MOCA Version 1 and 2 consisted of adding 200 mL (for Version 1) or 10 mL (for Version 2) of an aqueous solution

Table 37: List of the organics chosen for the preliminary analyses in the Mars Organic Carbon Analyzer (MOCA)

| Organic | # of Carbons | MW (g/mol) | Reason for Selection | Reference(s) |
|---------------|--------------|------------|--|---|
| Glycine | 1 | 75.07 | Interstellar molecule & Martian meteorites | [166] [167, 168, 169, 170, 171, 172] |
| Formate | 1 | 45.03 | Interstellar molecule | [166] |
| Methanol | 1 | 32.04 | Interstellar molecule | [166] |
| Acetate | 2 | 59.05 | Interstellar molecule | [166] |
| Acetone | 3 | 58.08 | Interstellar molecule | [166] |
| Alanine | 3 | 89.09 | Martian meteorites | [167, 168, 169, 170, 171, 172] |
| Serine | 3 | 105.09 | Martian meteorites | [172] |
| Aspartic Acid | 4 | 133.1 | Martian meteorites | [167, 169, 172] |
| Glutamic Acid | 5 | 147.13 | Martian meteorites | [167, 168, 169, 170, 172] |

containing the electrolyte and organic molecules to the solution reservoir along with a stir bar. The solution reservoir was then purged of CO₂ in the headspace by bubbling N₂ gas through the reservoir. The reservoir was then sealed tightly, placed on a stir plate and slow stirring began. The detector was plumbed into the system at the headspace of the reservoir and a background measurement was collected in order to determine the initial concentration of CO₂ in the system, ideally this value should be zero. The BDD and Pt electrodes were then connected to the power supply set at a constant current (in the range of -200 to 200 mA). The power supply was turned on starting the oxidation process. At the end of the experiment, or during set intervals throughout the experiment, the reservoir was opened to the detector and measurements were taken. The analysis terminated when there was no longer a change in the concentration of CO₂ as measured by the detector.

MOCA Version 3: Analysis in MOCA Version 3 consisted of adding 25 mL of an aqueous solution containing the electrolyte and organic molecules to the solution reservoir. The solution reservoir was then purged of CO₂ in the headspace by bubbling N₂ gas through the reservoir. The reservoir was then sealed and connected by silicone tubing to the pump and electrochemical cell in a closed-loop configuration. The detector was plumbed into the system at the headspace of the reservoir. The pump was run at a flow rate of roughly 5 mL per minute. Once flow had been established in the system, the solution reservoir was opened to the detector to collect a background measurement in order to determine the initial concentration of CO₂ in the system, ideally this value should be zero. The BDD and Pt electrodes were then connected to the power supply set at a constant current (in the range of -200 to 200 mA). The power supply was turned on starting the oxidation process. At

the end of the experiment, or during set intervals throughout the experiment, the reservoir was opened to the detector and measurements were taken. The analysis terminated when there was no longer a change in the concentration of CO₂ as measured by the detector. [152]

6.2.3 Oxidation Experiments

Due to the limitations of MOCA Versions 1 and 2 only experiments performed with MOCA Version 3 will be discussed. A variety of different oxidation experiments were performed using MOCA Version 3. While overall experimental parameters have been discussed previously, the specifics of each experiment is discussed below. The purpose of performing each experiment is also discussed.

For a majority of the oxidation experiments, a single test compound was chosen. Formate (HCOOH) was chosen as the test compound for several reasons. In addition to being a compound known to be oxidizable, [173, 174, 175] it has the ability to be monitored both by residual gas analyzer (RGA) or non-dispersive infrared (NDIR) gas analyzer for a direct measurement of CO₂ production and by ion chromatography (IC) for formate loss. Formate has a further advantage of containing only one carbon per molecule. Therefore, it is possible to test a carbon-13 labeled sample in which 99% of all the carbons were ¹³C.

Comparison of Working Electrodes: As discussed previously, platinum (Pt) is one of the most commonly used electrode materials. However, Pt is a Class 1 “active” electrode and prone to incomplete oxidation, while boron-doped diamond (BDD) is a Class 2 “non-active” electrode which favors complete oxidation to CO₂. In order to ensure that BDD is in fact the better electrode for the oxidation of organics, both BDD and Pt electrodes were

tested as a possible working electrode in MOCA.

The Pt and BDD electrodes were the same size and shape with a surface area of 0.66 cm². To compare the two electrodes, three different concentrations of the test compound formate, 0.19, 0.37, and 0.75 mmol formate (or ~90 mg/kg, 180 mg/kg and 360 mg/kg carbon, respectively) in 0.1 M H₃PO₄ background electrolyte was run at a current density of -173 mA/cm² for 50 minutes and the CO₂ produced was monitored by NDIR every ten minutes. First, MOCA was run with a BDD anode and Pt cathode and then the experiments were repeated with a Pt anode and Pt cathode. [152]

During later experiments it was discovered that the BDD electrode was having some problems with delamination from the underlying substrate material. Therefore, it was possible that some of the underlying tungsten wire was exposed during the above mentioned experiment. To determine if the W-substrate had any effect on the oxidation of organics, a tungsten electrode, type 1A, matching the substrate of the BDD electrode and measuring the same size, shape and surface area was also tested. [152]

Determination of Optimal Current Density: Experiments were performed to determine the optimal current density for the reaction of the test compound formate. The optimal current density is defined as the current density which provides the fastest rate at which organics are oxidized to carbon dioxide, *i.e.*, the optimal rate of oxidation. It was important to optimize the rate of oxidation so the experiment could be run as quickly as possible thus consuming less power and/or allowing more experiments to be performed in a given time frame.

The galvanostat used in this experiment, an EG&G Model 263A, has a current range from -200 to 200 mA. Thus, the current densities which could

be achieved ranged from -302 to 302 mA/cm². To determine the optimal current density, solutions containing 0.3735 mmol formate (or ~180 mg/kg carbon) in 0.1% H₃PO₄ background electrolyte were oxidized for 50 minutes at 11 different current densities ranging from -302 mA/cm² to 302 mA/cm². Data was collected every ten minutes by a residual gas analyzer set to monitor m/z 44 (the molecular weight of CO₂) to determine the rate of oxidation.

Carbon Isotopes: When using a residual gas analyzer (RGA), the concentration of CO₂ is not measured directly. Instead, the partial pressure of a specific mass to charge is monitored corresponding to the molecular weight of CO₂, m/z 44. Therefore, it was necessary to ensure that the increase in m/z 44 was indicative of a change in CO₂ caused by the oxidation of organic material and not for another interferent with the same mass to charge. To ensure the signal was due to the formation of CO₂, two equivalent oxidations were run using the test compound formate and ¹³C-labeled formate. For both tests, 0.125 mmol of either 99.9% ¹²C formate (equal to 60 ppm ¹²C formate) or 99% ¹³C formate (equal to 65 mg/kg ¹³C formate) in 0.1% H₂SO₄ background electrolyte were run at a current density of -173 mA/cm² for 2.5 hours. Data was collected every 30 minutes with a residual gas analyzer set to monitor both m/z 44, for ¹²CO₂, and m/z 45, for ¹³CO₂. During the analysis of ¹²C labeled formate, there should be an increase in m/z 44 and little to no increase in m/z 45 and vice versa for the ¹³C-labeled formate. [152]

In addition to using this test as a way of confirming the RGA was measuring the increase in CO₂ due to the oxidation of organic material by MOCA; an additional goal of the MOCA instrument was to not only detect TOC but also to detect carbon isotopes. A strong indication of past biological activity can be determined by quantifying the total amount of carbon and comparing the

$^{13}\text{C}/^{12}\text{C}$ isotopic ratio. This strategy has been used here on Earth to detect traces of ancient life. Thus, the test with the ^{13}C -labeled formate had more significance than just a check of the detection method.

If it is possible to oxidize and detect ^{13}C containing organics, the issue of isotopic fractionation becomes another possible concern. The kinetic isotope effect, a variation in the reaction rate when an atom is replaced by one of its isotopes, is a possibility. To date, no studies have been found which test whether ^{12}C and ^{13}C containing organics have similar or different rates of oxidation. Therefore, in the testing of formate versus ^{13}C -labeled formate, the rate of oxidation will also be measured to determine if there was a difference due to the kinetic isotope effect.

Comparison of Electrolytes: A variety of different background electrolytes were compared to determine if there was any effect on the rate of oxidation. The original electrolyte used in MOCA was 0.1 M sulfuric acid (H_2SO_4). Sulfuric acid was chosen to acidify the solution to below pH 2 to remove any inorganic carbon prior to oxidation. Sulfuric acid is commonly used to acidify samples prior to TOC analysis. However, when using a NDIR detector it is not wise to use sulfuric acid because it is possible that some SO_3 gas may be formed during oxidation which can cause a positive interference in the NDIR detector due to its similar detection properties to CO_2 . Therefore, another electrolyte, 0.1 M phosphoric acid (H_3PO_4) was explored. Phosphoric acid is another common acid used to acidify solutions prior to TOC analysis. [128]

To determine if the background electrolyte had an effect on the rate of oxidation of organics, 0.13 mmol formate (or ~ 230 mg/kg carbon) in either 0.1 M H_2SO_4 or 0.1 M H_3PO_4 was oxidized with a BDD anode at -173 mA/cm² for 2.5 hours. Data was collected every 30 minutes with a residual gas analyzer

set to monitor m/z 44 (the molecular weight of CO_2). Each oxidation was run three times and the average oxidation rate was determined with standard deviation. [152]

During the 2007 Phoenix Mars Mission the WCL discovered the presence of 0.6% perchlorate, most likely in the form of $\text{Mg}(\text{ClO}_4)_2$ or $\text{Ca}(\text{ClO}_4)_2$ (see Chapter 1). Therefore, 1% $\text{Mg}(\text{ClO}_4)_2$ was tested as a potential background electrolyte for MOCA. If $\text{Mg}(\text{ClO}_4)_2$ is a viable electrolyte and MOCA is used on Mars at a location where there is $\text{Mg}(\text{ClO}_4)_2$ in the soil, the instrument would not have to carry its own electrolyte and could operate with only a buffered solution. To test the viability of $\text{Mg}(\text{ClO}_4)_2$ as a background electrolyte, 0.37 mmol formate (or 675 mg/kg carbon) in 1% $\text{Mg}(\text{ClO}_4)_2$ was run at a current density of -173 mA/cm^2 for one hour. Data was collected every 15 minutes by a RGA set to monitor m/z 44 (the molecular weight of CO_2) to determine if the organic was oxidizable in this electrolyte and if so, determine the rate of oxidation. For comparative purposes, the same test was run in 0.1M H_2SO_4 and a combination of 1% $\text{Mg}(\text{ClO}_4)_2$ and 0.1M H_2SO_4 . These tests with all three electrolytes were repeated with a second organic compound, glutamic acid at a concentration of 0.03 mmol glutamic acid (or $\sim 62 \text{ mg/kg}$ carbon) to confirm whether or not more than just the test compound, formate, was oxidizable with the background electrolyte $\text{Mg}(\text{ClO}_4)_2$. [152]

Test of Various Organics: MOCA Version 3 is known to be capable of oxidizing the test compound, formate, completely to CO_2 . However, this is not the only organic of interest. Tests were therefore performed on all none of the organics listed in Table 37 to see if they could all be oxidized to CO_2 with this instrument. For this experiment, 0.125 mmol of one of the organics in Table 37 in 0.1% H_2SO_4 background electrolyte was oxidized for 2.5 hours

at -173 mA/cm^2 . Data was collected every 30 minutes with a RGA set to monitor m/z 44 (the molecular weight of CO_2) to determine if the organic was being oxidized to CO_2 and the rate of the oxidation. A blank containing no organic and only the 1% H_2SO_4 background electrolyte was oxidized under the same conditions to be used as a control. [152]

Target Detection Level: Not only is it important for MOCA to be capable of oxidizing a wide variety of organics, it is also necessary for this instrument to be able to oxidize and detect small levels of organics, *i.e.*, have a low limit of detection. A low detection limit is important because it is unknown how much organic material may be present on Mars and the lower the detection limit the greater chance organics can be positively detected. The detection limit will ultimately be dictated by the CO_2 detector coupled to MOCA. However, it first must be shown that MOCA is capable of oxidizing small quantities of organic material. As discussed previously, the mechanism of oxidation for this system is mass transfer limited, especially at low concentrations. Therefore, it is necessary to show that organics can still be oxidized and in a reasonable timeframe at low concentrations.

The target detection level for MOCA at this stage of development is the oxidation of 10 mg/kg of the various organics. Originally when testing to determine whether or not various organics were oxidizable, the amount of organic analyzed ranged from 160 to 736 mg/kg organic (or 60 to 300 mg/kg carbon) depending on the organic analyzed. Oxidation of each of the organics, except for methanol, was repeated at the same current density of -173 mA/cm^2 . However, this time 10 mg/kg of organic (or between 2 to 6 mg/kg carbon depending on the organic) was oxidized for 1 hour and the data was collected every 15 minutes for one hour by RGA set to monitor m/z 44 (the molecular

weight of CO₂) to determine if any of the organic was oxidized to CO₂ in this timeframe. The tests were repeated under the same conditions with 225 mg/kg organic (or between 60 to 140 mg/kg carbon depending on the organic) for comparison. [152]

6.3 Results and Discussion

The results of the cyclic voltammetry studies on the organics of interest from Table 37 and the oxidation experiments conducted with MOCA Version 3 are discussed below. During the oxidation experiments, some issues and set-backs were encountered. Therefore, a description of these problems and suggestions for possible solutions will also be discussed.

6.3.1 Cyclic Voltammetry

Cyclic voltammograms were taken of the nine organics listed in Table 37 using both glassy carbon (GC) and boron-doped diamond (BDD) working electrodes. As seen in Figure 57, no oxidation peaks were present in either the oxidative or reductive scans from -0.3 to 2 V for the glassy carbon electrode in a solution of 25 mM sodium formate and 0.1 M sulfuric acid. The same was true for the BDD electrode. Likewise, all of the other eight organics tested also did not reveal any peaks in their CV scans from -0.3 to 2 V using either the GC or BDD working electrodes. This result was consistent with previous results reported in the literature. [173] Cañizares et al. reported the presence of a shoulder in the CVs of carboxylic acids, such as formate and acetate, that overlapped the region of oxygen evolution at about 2.3 V vs. SHE indicating oxidation of these compounds in the region of water instability. [174] However, this could not be seen in the voltammograms herein due to the limitations of the voltage range of the potentiostat. These results were consistent with the

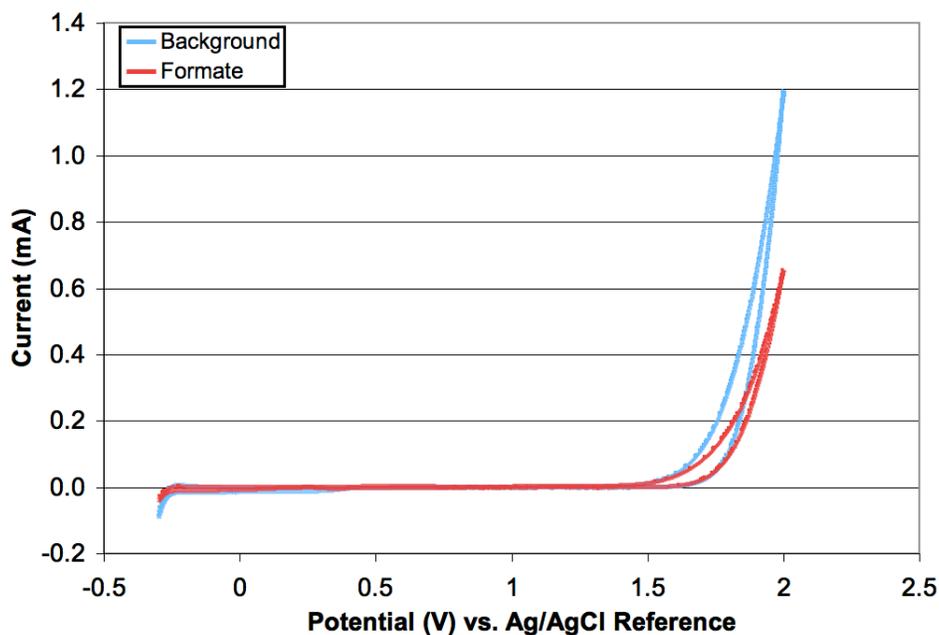


Figure 57: CV of 0.1 M H_2SO_4 both with and without 25 mM sodium formate using a GC working electrode, Pt counter electrode and Ag/AgCl reference electrode. (Scan rate = 50 mA/sec, Sample interval = 1, Sensitivity = 1 mA/V)

theory for an indirect oxidation mechanism. Since there were no anodic peaks present below the region of oxygen evolution (Equation 20) for these nine organics, the oxidation of these compounds can only take place in the potential region of water discharge, *i.e.*, hydroxyl radicals are necessary which confirmed an indirect mechanism of oxidation. [147]

6.3.2 Oxidation Experiments

Two different working electrodes were tested to determine if BDD is the electrode of choice for MOCA. The optimal current density was then determined followed by tests to ascertain if the amount of organic has an effect on the rate of oxidation. Nine organics likely to be present on Mars were tested to see if this instrument could oxidize a variety of organic compounds. Three different electrolytes were then tested as well as the instrument's ability to oxidize

both ^{12}C and ^{13}C -containing molecules. The results from all of these oxidation experiments are presented below.

Comparison of Working Electrodes: Both Pt and BDD electrodes were tested to confirm that using a BDD working electrode would provide a more complete oxidation of organics as well as a faster rate of oxidation. Each electrode was tested at three different concentrations of the test compound, 0.19, 0.37, and 0.75 mmol formate (equivalent to ~ 90 mg/kg, 180 mg/kg and 360 mg/kg carbon, respectively), in 0.1 M H_3PO_4 background electrolyte. Figure 58 shows the normalized percent of formate oxidized for both electrodes when oxidizing 0.75 mmol formate. [152]

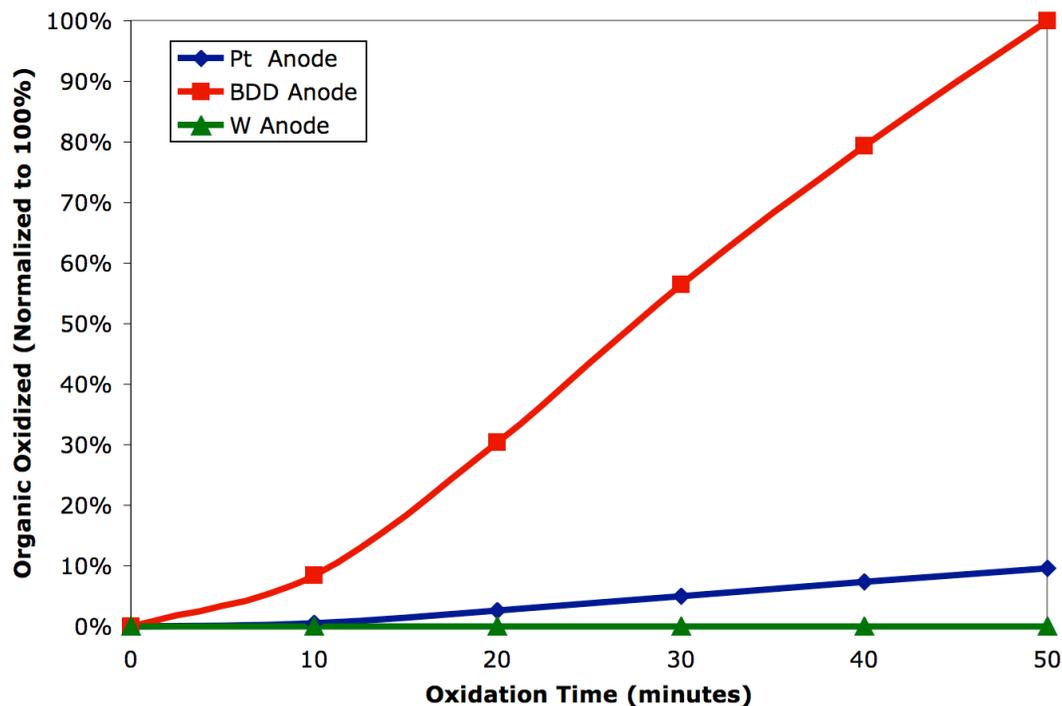


Figure 58: Organic oxidized (normalized to 100%) versus oxidation time for three different anodes in MOCA: Pt, BDD, and W. Solution: 0.75 mmol formate (or 360 mg/kg carbon) in 0.1 M H_3PO_4 . Current Density: -173 mA/cm^2

The percent formate oxidized was normalized to 100% because a complete ($> 99\%$) oxidation to CO_2 was not achieved by either anode tested in the 50

minute timeframe of the oxidation experiment. There was a large difference in performance of the two electrodes. The BDD anode oxidized at a rate of ~ 10 times faster than the Pt electrode when oxidizing the samples containing 0.75 mmol formate (or ~ 360 mg/kg carbon). The trend was similar with lower concentrations of formate, with the BDD electrode oxidizing at a faster rate than the Pt electrode. However, the difference in rates become closer together as the amount of formation in solution decreased. The solution of 0.37 mmol formate (or ~ 180 mg/kg carbon) exhibited a 7-times greater rate of oxidation when using the BDD electrode and the 0.19 mmol formate (or ~ 90 mg/kg carbon) had only a 4.8-times greater rate of oxidation when using the BDD electrode. Overall, this test confirmed the use of a BDD electrode in MOCA will result in a faster rate of oxidation. [152]

Additionally, when the W substrate material was tested there was no oxidation of formate with this electrode (Figure 58). Thus if any substrate material was exposed during the initial tests it would not help oxidize the organics. In fact, exposed W substrate would actually hinder the oxidation with the BDD electrode due to the decrease in BDD surface area available for oxidation to occur. If any W substrate was exposed during the above experiments, the difference in increased oxidation rate BDD as compared to the Pt electrodes in MOCA would be even greater than the amounts presented here. [152]

Determination of Optimal Current Density: Eleven different current densities ranging from -302 to 302 mA/cm² were tested. Figure 59 shows the percent of formate oxidized as a function of current density. The percent formate oxidized was normalized to 100% because a complete ($> 99\%$) oxidation of formate to CO₂ was not achieved at any of these current densities after 50 minutes. From this experiment it was determined the optimal current den-

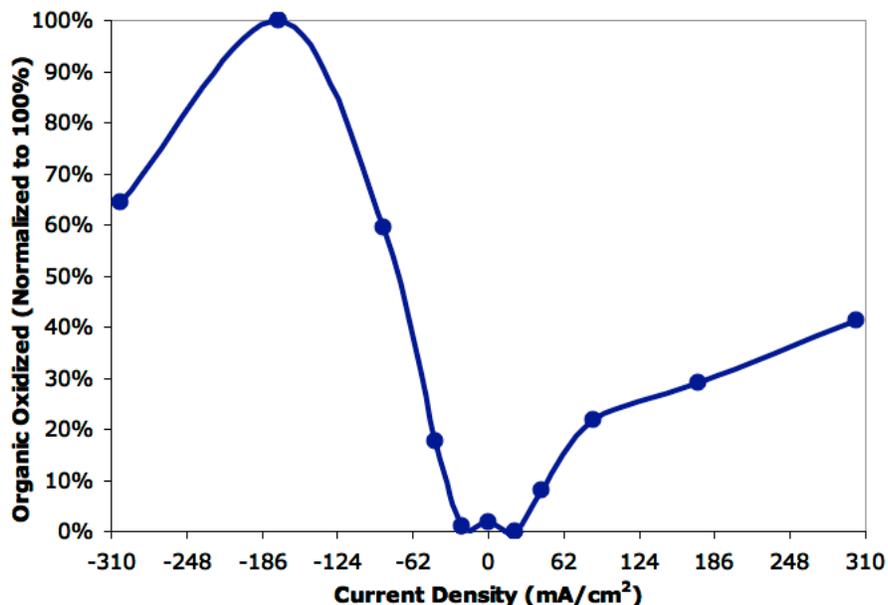


Figure 59: Organic oxidized (normalized to 100%) as a function of the applied current density (in mA/cm²). Solution: 0.3735 mmol formate (or ~180 mg/kg carbon) in 0.1 M H₃PO₄

sity for the oxidation of the test compound formate was -173 mA/cm². This current density was therefore used for the remainder of the experiments performed. A wider range of current densities may be possible though the use of a different power supply. Therefore, this optimization should be repeated if/when a different power source is selected.

Carbon Isotopes: Monitoring by RGA, using m/z 44 for ¹²CO₂ and m/z 45 for ¹³CO₂, was shown to be effective for the detection of the ¹²CO₂ and/or ¹³CO₂ being produced from the oxidation of organics and that these m/z ratios were not detecting some other species. When 99.9% ¹²C formate was tested, there was an increase in m/z 44, corresponding to ¹²CO₂ and very little increase in m/z 45, corresponding to ¹³CO₂ (Figure 60 top). Likewise, when 99% ¹³C formate was being tested, there was an increase in m/z 45, corresponding to ¹³CO₂, and very little increase in m/z 44, corresponding to ¹²CO₂ (Figure 60

bottom). The increase seen in the the other carbon isotope of CO₂ is the result of the samples not being 100% either ¹²CO₂ or ¹³CO₂. [152]

In Figure 60, the CO₂ produced is normalized to 100% because a complete (> 99%) oxidation to either ¹²CO₂ or ¹³CO₂ was not achieved in the 2.5 hour timeframe of the oxidation. Due to this fact, it cannot be seen from this figure if there was a difference in oxidation rate between an organic molecule containing ¹²C and ¹³C. However, there was found to be a difference in the rate of oxidation between ¹²C formate and ¹³C-labeled formate, with the ¹³C-labeled formate being slower to oxidize than the ¹²C formate. There was slightly more carbon to oxidize in the ¹³C-formate sample (65 mg/kg ¹³C versus only 60 mg/kg ¹²C). Despite the small difference in carbon concentration between the two tests, this result still suggests there is the possibility for isotopic fractionation and the presence of ¹³C organics may necessitate longer reaction times to ensure that all carbon is oxidized. Future analyses verifying this finding and testing differing ratios of ¹²C to ¹³C in the organics is planned for future work. [152]

Comparison of Electrolytes: Two different electrolyte solutions, 0.1 M H₂SO₄ and 0.1 M H₃PO₄, were tested to determine if there was any difference in reaction rate of the test compound formate at a current density of -173 mA/cm². Both electrolytes were tested three times and the average rate of oxidation was similar for both electrolytes within their standard deviations. Next, MOCA was tested to determine if 1% Mg(ClO₄)₂ was a viable background electrolyte for the oxidation of organics. Two organics were tested, formate and glutamic acid. Both organics were oxidized and their corresponding CO₂ was detected when using 1% Mg(ClO₄)₂ as the background electrolyte. [152]

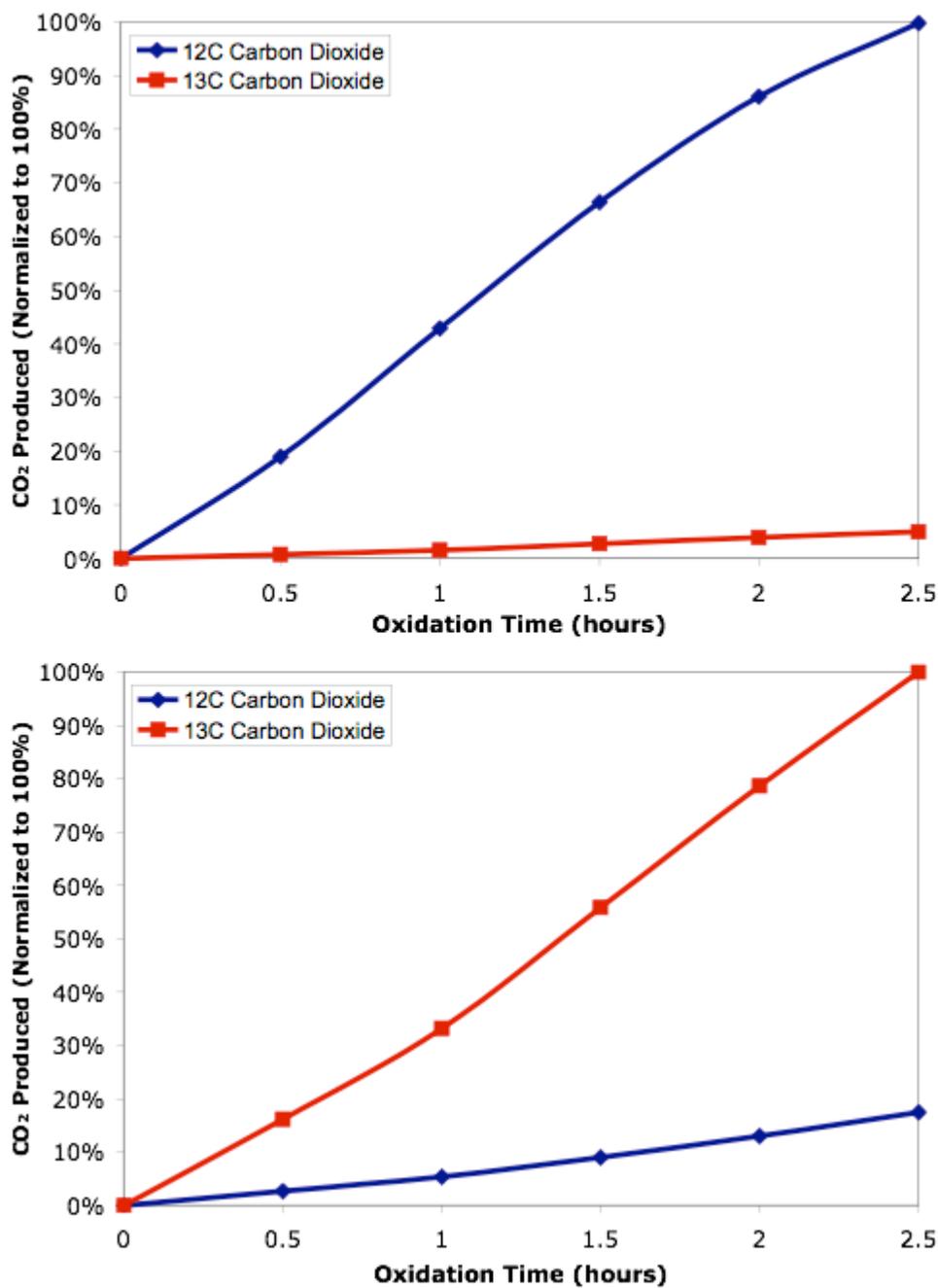


Figure 60: Percent organic oxidized, normalized to 100%, versus oxidation time for: 99.9% ¹²C formate (top) and 99% ¹³C formate (bottom). Solution: 0.125 mmol ¹²C-formate or ¹³C-formate (or 60 mg/kg ¹²C or 65 mg/kg ¹³C) in 0.1 M H₂SO₄. Current Density: -173 mA/cm²

As seen in Figure 61, there is a noticeably less formate and glutamic acid oxidized using the a background electrolyte of 1% $\text{Mg}(\text{ClO}_4)_2$ as compared to 0.1 M H_2SO_4 . Test performed in the presence of both 1% $\text{Mg}(\text{ClO}_4)_2$ and 0.1

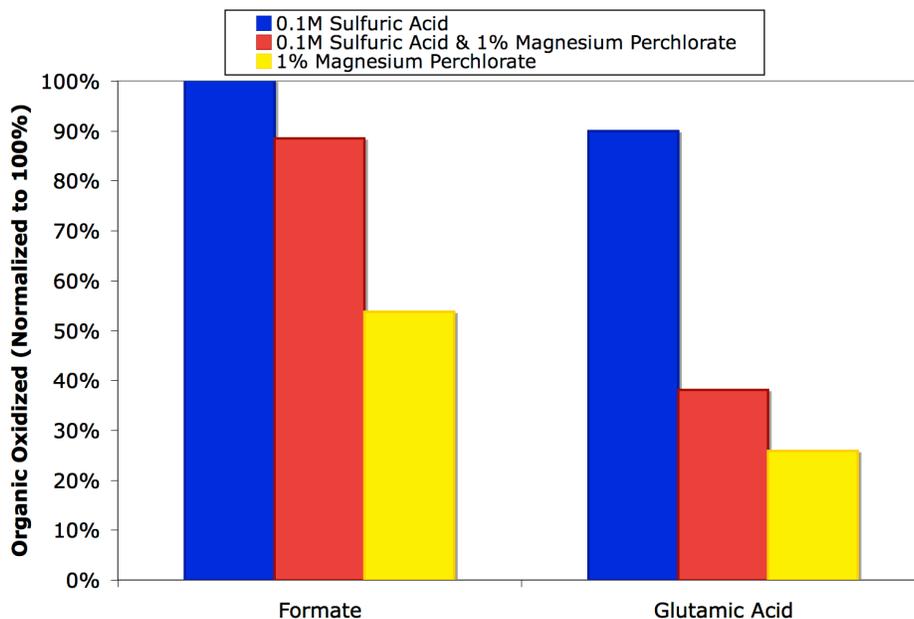


Figure 61: Organic oxidized (normalized to 100%) for formate and glutamic acid in: 0.1 M H_2SO_4 , 0.1 M H_2SO_4 & 1% $\text{Mg}(\text{ClO}_4)_2$, and 1% $\text{Mg}(\text{ClO}_4)_2$. Solution: 675 mg/kg formate or glutamic acid in each of the background electrolytes. Current Density: -173 mA/cm^2

M H_2SO_4 increased the amount of both organics oxidized in the timeframe of the experiment as compared to 1% $\text{Mg}(\text{ClO}_4)_2$ only but the percents oxidized were still not as high as when the electrolyte was 0.1 M H_2SO_4 only. [152]

From this study it was determined that using 1% $\text{Mg}(\text{ClO}_4)_2$ in place of 0.1 M H_2SO_4 or H_3PO_4 it is still possible to oxidize organics to CO_2 with MOCA. However, the use of 1% $\text{Mg}(\text{ClO}_4)_2$ reduces the rate of oxidation compared to either 0.1 M H_2SO_4 or H_3PO_4 , and being non-acidic does not remove unwanted, dissolved CO_2 in solution prior to analysis. Thus, even though the acid is not indispensable, the inclusion of a pH ~ 3 buffer is desirable in order to equilibrate the system in terms of CO_2 and provide for detection of specifically organic

CO₂, and ensuring the lowest possible limits of detection. [152]

Test of Various Organics: In addition to formate, eight other low molecular weight (1 to 5 carbon) organic molecules were oxidized using MOCA Version 3. A blank was run, which consisted of only the background electrolyte, which showed no oxidation; while all nine organics were shown to be oxidizable by MOCA. Figure 62 shows the normalized percent organic oxidized for all nine organics as a function of oxidation time. [152]

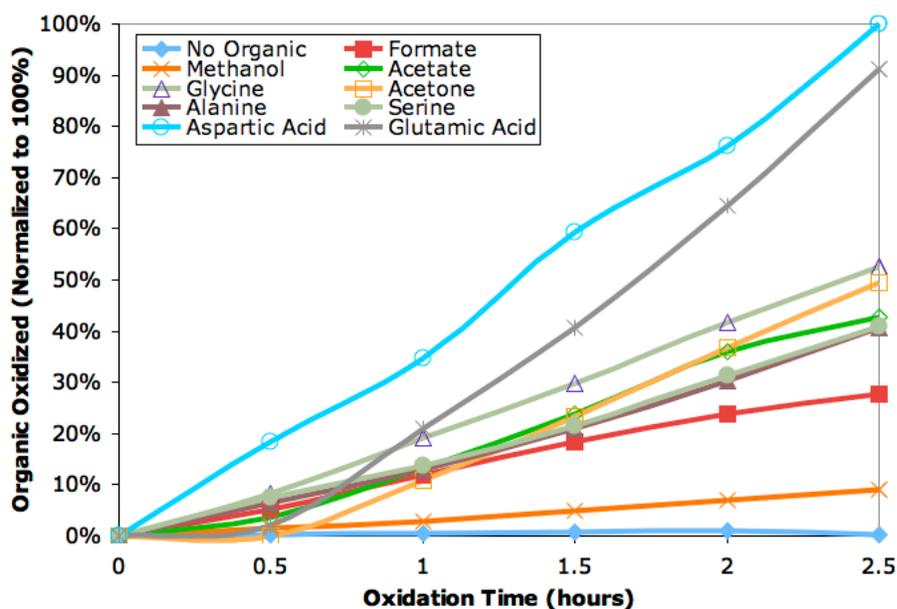


Figure 62: Organic oxidized (normalized to 100%) versus oxidation time for nine different organic molecules. Solution: 0.125 mmol organic (various concentrations of carbon depending on the organic) in 0.1 M H₂SO₄. Current Density: -173 mA/cm²

The percent organic oxidized was normalized to 100% because a complete (> 99%) oxidation to CO₂ was not achieved by any of the organics tested in the 2.5 hour timeframe of the oxidation. Methanol showed the slowest rate of oxidation and aspartic acid showed the fastest rate of oxidation. There was no noticeable trend in rate of reaction based on number of carbons, molecular weight or functional groups present. [152]

Through this experiment it was shown that MOCA is capable of oxidizing all the organics listed in Table 37. [152] Future testing will include an even larger variety of organics including refractory organics (*e.g.*, humic acid) as well as organics in samples collected from Mars analog environments, such as the Atacama Desert or the McMurdo Dry Valleys of Antarctica.

Target Detection Level: To test the detection of MOCA at the 10 mg/kg organic level, eight organics from Table 37 were oxidized at the 10 mg/kg organic level. The MOCA was run for one hour to see if any CO₂ was detected in this timeframe, indicating that even at this low level of organics oxidation was still possible at a reasonable rate. For all eight organics tested there was some production of CO₂ within the one hour timeframe. Thus, it was possible to oxidize organics as low as 10 mg/kg starting concentration. [152]

As expected, the rate of oxidation slowed as the concentration of organics decreased. The same eight organics were run under identical conditions at a starting concentration of 225 mg/kg. Figure 63 shows the percent organic oxidized in one hour for both starting concentrations. [152]

The data was normalized to the fastest rate of oxidation, glutamic acid at 225 mg/kg starting concentration. Oxidation at a starting concentration of 225 mg/kg oxidized at a rate of 11 to 24 times faster than the same organic at the 10 mg/kg level. Thus, while it is possible to oxidize at these lower starting levels of organics, the experiment time, which is already slow when compared to commercial TOC detection methods becomes, even slower. [152] One potential solution to increase the oxidation rate at these low concentrations would be to increase the surface area of the BDD anode. The surface area of the BDD anode for these tests was only 0.66 cm², therefore, future testing will include reconfiguring the MOCA electrochemical cell to support a BDD anode with a

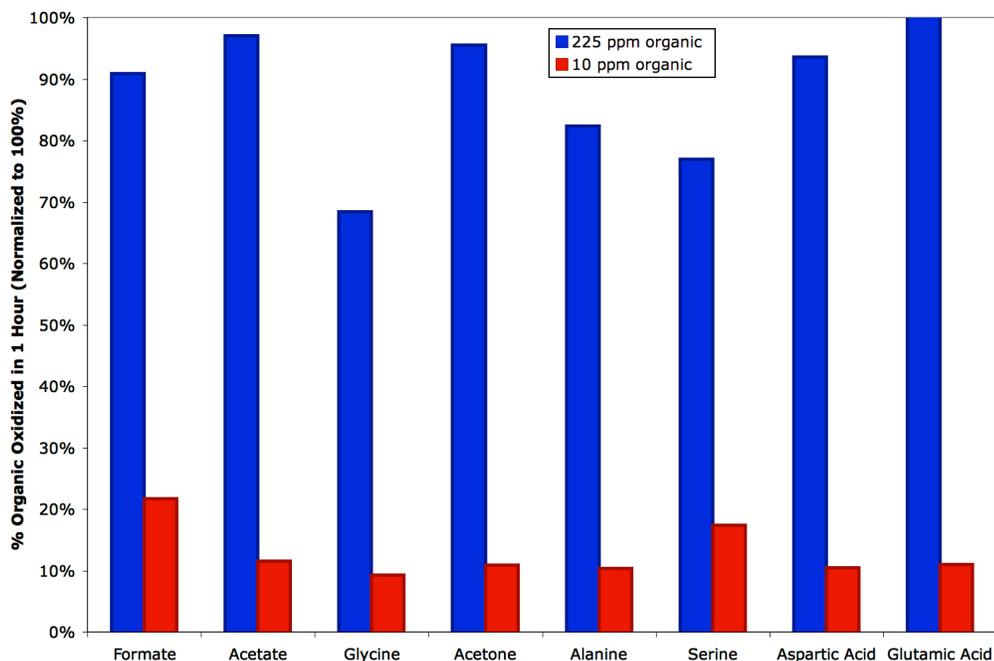


Figure 63: Percent organic oxidized in 1 hour (normalized to 100%) for eight different organic molecules at the 10 mg/kg and 225 mg/kg levels. Solution: 10 or 225 mg/kg organic in 0.1 M H₂SO₄. Current Density: -173 mA/cm²

larger surface area.

6.3.3 Setbacks for MOCA

In the fabrication and testing of MOCA several set-backs were encountered. When testing MOCA Version 1 and 2, it was determined these set-ups were incapable of being sealed tightly enough to prevent gas leakage. As CO₂ was produced during the oxidation process, in addition to H₂ and O₂ gas from the oxidation of water (Equation 20), the pressure inside MOCA would build rapidly and cause leakage at one or both of the stopcock adaptors. The problem of gas leakage was solved through a complete re-design of MOCA to Version 3 in which a solution reservoir with headspace for gas collected was separate from the electrochemical cell where oxidation of organics occurs. Additionally, Version 3 was better constructed to prevent gas leakage.

The biggest set-back to the testing of MOCA involved the BDD anodes. The electrodes used for MOCA Version 2 were BDD coated on a niobium substrate measuring 1 mm in thickness (Figure 55). There were problems with the coating of these electrodes. When the substrate was placed in the CVD chamber, one side was coated with BDD and then the substrate was turned over and the other side was coated. Two issues arose from this method of deposition which was evident when they were received from the manufacturer. First, the two sides did not receive the same thickness of coating, as evidenced from the difference in color between the two sides. Second, there was difficulty in coating the edges of the electrode which led to incomplete coating of the entire surface. These issues with coating were overcome by switching to a different size and shape of electrode for MOCA Version 3 (Figure 56). The substrate material for the BDD electrodes in this set-up was 0.5 mm diameter tungsten wire. By switching to this design it was possible for the manufacturer to coat the entire surface with a BDD layer of uniform thickness.

However, there were still some inconsistent results seen when testing identical experimental conditions with these BDD coated W-wire electrodes which were grown in different batches, which is presumably the result of slightly different quality growth from batch to batch. The bigger issue to arise with these BDD coated W-wire electrodes was a problem of delamination, BDD coating separating from the underlying substrate. Therefore, even though these electrodes were completely coated, the coating was not well adhered.

The use of metal substrates, such as the Nb and W used in these electrodes, are known to become embrittled during the diamond coating process. Therefore, it is possible that small pinholes developed in the coating which could cause the delamination of the electrode with repeated use, especially at higher currents and in the presence of acidic solutions such as the 0.1 M

H₂SO₄ or H₃PO₄ used in the majority of these experiments. Once the BDD coating began to come off the anode it was still usable, but the effectiveness was decreased and eventually all the coating was gone and the W-wire itself has been proven to be ineffective in the oxidation of organics, thus completely stopping the oxidation process.

Currently, one of the makers of these BDD electrodes, the Diamond Lab in the Department of Chemical Engineering at Case Western University are in the process of investigating a different substrate, a metal alloy, which appears to remain more docile after diamond coating and therefore may be a better substrate for diamond growth and a possible solution to the problem of delamination. Likewise, another avenue to explore is the use of BDD electrodes grown on a silicon substrate. The issue with silicon as a substrate material has always been its brittleness. However, because of the design of the electrochemical cell, the electrode would be well protected from breakage. Therefore, future testing of MOCA will use BDD electrode on silicon provided by Fraunhofer USA, Center for Coatings and Laser Applications at Michigan State University.

6.4 Conclusions

The search for the presence of organics on Mars has been ongoing for the past 35 years. Both the Viking missions and Phoenix's TEGA have failed to detect organics in the Martian soil using pyrolysis for the volatilization of organics followed by detection with mass spectrometry. However, the next two upcoming missions, MSL and ExoMars, have also chosen to search for the presence of organics using similar methods with their SAM and MOMA instruments. A potential drawback to the use of this method of volatilization and detection is the presence of the 0.6% ClO₄⁻ in the soil discovered by

Phoenix's WCL (see Chapter 1) which is capable of oxidizing organics under high temperature conditions. Therefore, a completely different approach to organics detection has been suggested in the usage of a total organic carbon (TOC) analyzer.

TOC analyzers are used on Earth primarily for the detection of contaminants in water sources. Commercially available TOC analyzers have also been used to determine TOC in extreme environments, such as the McMurdo Dry Valleys and the Atacama Desert. However, these commercially available TOC analyzers are not suitable for *in situ* analysis in these environments due to their size, weight and high power requirements. Therefore, a novel *in situ* TOC analyzer, the Mars Organic Carbon Analyzer (MOCA), is being developed as a means of detecting and quantifying *in situ* organic carbon in soils both here on Earth and on Mars.

MOCA, in its current state of design uses a boron-doped diamond (BDD) anode to electrochemically oxidize organics to CO₂ which is then detected and used for the quantification of TOC. BDD is the anode of choice, in spite of the current issues with delamination due to its ability to oxidize a test organic, formate, at a rate ten-times faster than a Pt anode. Through preliminary oxidations, the optimal current density for the oxidation of organics to CO₂ was determined. Using this current density, MOCA was shown to be capable of oxidizing a variety of low molecular weight (1 to 5 carbon) organics at starting concentrations as low as 10 mg/kg organic. MOCA has also shown the ability to oxidize ¹³C organics in addition to ¹²C organics which is important because a strong indication of past biological activity can be determined by quantifying the total amount of carbon and comparing the ¹³C/¹²C isotopic ratio. Likewise, unlike other organic detectors which are hindered by the presence of 0.6% Mg(ClO₄)₂ in the Martian soil, this compound's presence

is beneficial for MOCA. MOCA has shown the ability to use ClO_4^- as the background electrolyte during the oxidation of organics, meaning to operate MOCA on Mars only a low pH buffer aqueous solution would be necessary in place of more harmful chemicals. [152]

MOCA is currently at a NASA technology readiness level (TRL) 4, meaning the instrument has been tested in a laboratory environment. In its current state, MOCA has proven to be a powerful instrument for the detection of TOC on Mars with its capability to use what is already known to be present in the Martian soil, 0.6% ClO_4^- , and its ability to oxidize and detect carbon isotopes. Still, this instrument still has a ways to go before it can be commercialized for use in environmental *in situ* analysis on Earth or be integrated into a future mission to Mars. Plans for the future testing and modifications to MOCA to get the instrument from a TRL 4 (laboratory tested) to a TRL 6 (shown to be operational in a Mars ambient environment) are discussed below.

6.5 Future Directions

The ultimate goal is to fabricate a fully integrated instrument capable of performing organic analyses on planetary surfaces. MOCA in its current embodiment is at a NASA technology readiness level (TRL) 4. The next projected milestone for this work is to bring MOCA from a TRL 4 to a TRL 6. Plans to reach this next milestone are discussed below along with alternative approaches to the possible configuration of MOCA.

In its current state, MOCA is at a TRL 4 meaning the instrument has been tested in a laboratory environment and has show the capability of oxidizing several low molecular weight (1 to 5 carbon) organic molecules to CO_2 . Once the current BDD electrode delamination problems are overcome an additional step in this TRL is to characterize the TOC detection with a wider variety of

organics including refractory organics (*e.g.*, humic acid) as well as organics in samples collected from Mars analog environments, such as the Atacama Desert or the McMurdo Dry Valleys of Antarctica.

At the next level, TRL 5, the MOCA will be tested in the field in a Mars analog environment such as the MDV or the Atacama Desert. Before MOCA can be tested in the field, modifications must be made to the current design. The electrochemical cell, solution reservoir and pump are all field ready, being small and lightweight. However, the pump would require a small power supply. The galvanostat can easily be replaced with a programmable power supply capable of supplying the -100 to -500 mA of current. As for a CO₂ detector, the RGA is too large, heavy and power hungry to be practical for a field test, but the NDIR is small, lightweight and only requires an additional power supply capable of supplying an input voltage of 12-30 VDC and a laptop for running the detector's software. With these changes the MOCA could be easily transported to and powered in the field as a small suitcase sized device.

After field testing, TRL 6 requires the MOCA to be tested in a Mars ambient environment at temperatures in the -30 to -100 °C range and an atmosphere of 7-10 mbar composed of 95.32% CO₂. To achieve this level, significant modifications must be made to MOCA. Currently MOCA is designed to operate at Earth ambient conditions of 20-25 °C and 1 atm composed of only 0.039% CO₂. Operation on Mars would require the electrochemical cell, reservoir and liquids to be heated to at least 5 °C. Since this is similar to the requirements for the WCL aboard Phoenix, the appropriate changes can be made to MOCA design to satisfy these conditions. Additional modification to MOCA can also be made to account for the background of 10 mbar CO₂ on Mars. A suitable inert gas such as nitrogen or argon would be needed to purge MOCA after the insertion of the soil sample to substantially lower the starting

background level of CO₂ in the system prior to analysis. However, the detection of CO₂ produced by oxidation of the organics, measured as a change in signal, could be accomplished as long as the background CO₂ levels remained relatively constant and were monitored as sufficient levels to compensate for any changes.

Additional work on MOCA include determining a method for sample addition. such as the integration of MOCA with the Automated Sample Processing System (ASPS) currently under development at JPL. The ASPS would process the soil, extract the organics and provide the appropriate volume of solution to MOCA. Alternative approaches to the possible configuration of MOCA will also be explored such as integrating the electrochemical cell with the solution reservoir, more like Versions 1 and 2 and similar to the WCL aboard Phoenix, and using a stirrer to mix the solution. By integrating the solution, it would negate the need of a pump to circulate solution cutting back on the instrument's complexity, size and weight. Also, like WCL, an array of other sensors could be added to MOCA to monitor additional chemistry occurring during the oxidation process.

Changes to MOCA's detection method will also be explored. While the RGA works well in the lab and the NDIR would be effective in field testing, the the use of a tunable diode laser (TDL) spectrometer for the detection of gaseous CO₂ would be better suited for space and is capable of providing ¹³C/¹²C ratios. The integration of a liquid-phase CO₂ detector would be advantageous. Possibly, a CO₂ ion selective electrode could be used if the detection limits of these sensors were sufficiently low to measure small changes in CO₂. By changing the method of detection, the limits of detection can be lowered increasing the overall sensitivity of MOCA.

Overall Conclusions

In this work soils from three extreme environments, Mars (Chapter 1), the McMurdo Dry Valleys (MDV) of Antarctica (Chapters 2 and 3) and the Atacama Desert in Chile (Chapter 4), were analyzed for their geochemical properties of soil pH, conductivity, ionic strength, and soluble ion content. In addition to gaining more insight into the soil chemistry of two well known but little studied extreme environments on Earth, comparisons could be drawn between these environments and the planet Mars. Information about the soil chemistry on Mars is extremely limited and there are few opportunities to perform analysis *in-situ* on the Martian surface. Therefore, determining suitable Mars analog environments or its soils are crucial to testing novel next generation instrumentation for Mars exploration.

In Chapters 2 and 3, the geochemical properties of the soil from the coastal thaw zone (CTZ) and the stable upland zone (SUZ) were compared to the soil from the Phoenix lander site in the north polar region of Mars. While the soils from both zones were similar to the Martian soil, the soils from the SUZ were found to be a closer match than those from the CTZ. In Chapter 4, the geochemical properties of the soil from three locations within the Atacama Desert, AT10 OE, AT10 6 and AT10 P, were compared to the soil at the Phoenix lander site. The soils collected from all three locations within the Atacama were comparable to the Martian soil. Appendix J compiles the data from all three extreme environments and compares the geochemical properties of the top 5 cm of soil from four different locations, the Phoenix Lander site on Mars, the CTZ in the MDV, the SUZ in the MDV and the linear transect, AT10 P, in the Atacama Desert.

All four locations were found to possess a similar soil pH, when measuring the soil leachate. The pH was in the neutral range averaging with standard

deviation from slightly acidic to slightly basic (a range from pH 6 to 8). Likewise, the electrical conductivity of the soil, when measuring the soil leachate, was also similar for all environments. The average electrical conductivity with standard deviation was on the same order of magnitude for the Martian, Atacama and SUZ soils. The soil from the CUZ was an order of magnitude lower than the other locations. However, this can be explained by the increased moisture at this location. Of these four locations the CTZ is the least arid and therefore the rate of dissolution to the rate of deposition is greatest in this zone, resulting in a lower electrical conductivity. [51]

There were similar ions found in the soil in all four of these locations. The biggest differences in the type of ions present was the presence of Li^+ in the soil from the Atacama Desert (though it should be noted that measurable quantities of Li^+ were only seen in two of the three locations sampled and therefore is not ubiquitous to the soil in this extreme environment), and the lack of any measurable quantity of NH_4^+ or NO_3^- in the Martian soil at the Phoenix lander site. [51] In the case of NO_3^- , this ion could not be detected on Mars with the WCL [6], but there is some evidence for nitrates on Mars. [21] If present at the Phoenix lander site, the measured conductivity would be consistent with $[\text{NO}_3^-] < 1 \text{ mM}$ in the soil leachate. [52]

The other ions, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} and ClO_4^- were present in measurable quantities in all four extreme environment locations. The concentration of most ions present at all four locations varied by one to two orders of magnitude across all four locations. The only exception was ClO_4^- which appeared in concentrations three to four orders of magnitude greater in the Martian soil than in the soils from the extreme environments on Earth. Comparison of the ion to ion ratios revealed differences for most ratios in all four locations, indicating that in each environment there are different accumulation

and depletion pathways for the species. [51]

The geochemical properties of the soils from all three extreme environments were found to be similar. Therefore, these studies confirmed that both the Atacama Desert and the MDV possess good Mars analog soils, and are suitable for the testing of novel next generation instrumentation for Mars exploration. There was no perfect match of any of the soils analyzed to the Martian soil at the Phoenix lander site. However, it was shown that soils from neither extreme environment were drastically different from Mars, with variations in geochemical properties being just as large between soils from the Atacama and the MDV as between either of these environments and Mars. Overall, when looking not only at the soil's geochemical properties but also other factors such as climate and geomorphology, the SUZ of the MDV appears to be the closest match to the north polar region of Mars. [51]

There is still much to learn about the extreme environments discussed herein: the McMurdo Dry Valleys of Antarctica, the Atacama Desert in Chile and Mars. From this study, the soil from the SUZ of the MDV have been found to possess the geochemical properties most similar to the soil from the north polar region of Mars at the Phoenix lander site. However, the soils from all extreme environments varied widely and there is nothing to support the assumption of a homogeneous soil at any of these locations. Additionally, there is a geochemical property of the soil that has yet to be compared between these environments, the organic content. Thus, with each new visit to these locations and with every analysis performed on the soils therein, new information will be gathered to expand our understanding of these unique and extreme places.

Appendix A: Abbreviations

- **BDD:** boron-doped diamond
- **BV:** Beacon Valley
- **C, C, and C:** calibration, characterization and cataloging
- **CTZ:** coastal thaw zone
- **CV:** cyclic voltammetry
- **CVD:** chemical vapor deposition
- **EDX:** energy dispersive x-ray spectroscopy
- **EPA:** Environmental Protection Agency
- **ESA:** European Space Agency
- **FU:** flight unit
- **GC-MS:** gas chromatograph mass spectrometry
- **GWB:** Geochemist's Workbench ®
- **HF-CVD:** hot filament chemical vapor deposition
- **IC:** ion chromatography
- **IMZ:** inland mixed zone
- **IPY:** International Polar Year
- **ISE:** ion selective electrode
- **JSC:** Johnson Space Center
- **LD-MS:** laser desorption mass spectrometry
- **MECA:** Microscopy, Electrochemistry and Conductivity Analyzer
- **MDV:** McMurdo Dry Valleys
- **MOA:** Mars Organic Analyzer
- **MOCA:** Mars Organic Carbon Analyzer
- **MOD:** Mars Organic Detector
- **MOI:** Mars Organic Instrument
- **MOMA:** Mars Organic Mass (or Molecule) Analyzer

- **MPA-CVD:** microwave plasma assisted chemical vapor deposition
- **MSL:** Mars Science Laboratory
- **NDIR:** non-dispersive infrared
- **NPOC:** non-purgable organic carbon
- **PAH:** polycyclic aromatic hydrocarbons
- **RGA:** residual gas analyzer
- **SAM:** Sample Analysis at Mars
- **SEM:** scanning electron microscopy
- **SUZ:** stable upland zone
- **TB:** testbed
- **TC:** total carbon
- **TEGA:** thermal and evolved gas analyzer
- **TIC:** total inorganic carbon
- **TIC-TOC** Total Organic Carbon - Total Organic Carbon Analyzer
- **TOC:** total organic carbon
- **TV:** Taylor Valley
- **UV:** University Valley
- **VOC:** volatile organic carbon
- **VV:** Victoria Valley
- **WCL:** Wet Chemistry Laboratory
- **WV:** Wright Valley

Appendix B: Definitions

- **Caliche:** a conglomerate of insoluble and barren minerals such as breccia, sands, and clays, firmly cemented by soluble oxidizing salts that are predominantly sulfates, nitrates, and chlorides of sodium, potassium, and magnesium with significant quantities of borates, chromates, chlorates, perchlorates and iodates. [95]
- **Caliche Blanco (or white caliche):** any nitrate-bearing mineral that is composed entirely of soluble salts [96]
- **Dry Permafrost:** material that remains below 0°C for two or more years in succession but has insufficient interstitial moisture to be cemented. [Ferrians 1969] [40]
- **Frozen Ground:** similar in meaning to permafrost but commonly implies the presence of ice [35]
- **Ice-cemented:** permanently frozen material such as till in which all the interstices between the solids are filled with ice. This material is very tough and almost impossible to break up in the field [35]
- **Martian Soil:** any loose, unconsolidated materials that can be distinguished from rocks, bedrock, or strongly cohesive sediments. No implication of the presence or absence of organic materials or living matter is intended. [176]
- **Patterned Ground:** patterns delineated by distinct stone and soil domains visible at the ground surface formed by freezing and thawing of soil layers in polar and high alpine environments. Patterns include: circles, labyrinths, stripes and polygons. [177]
- **Permafrost:** any soil or subsoil which remains below freezing for a long time - years to thousands of years. Material which is permanently below the freezing point but which contains insufficient ice to harden or cement it. (there is no regard to texture, degree of compaction, water content or lithological character of the material) [35]
- **Regolith:** the layer of loose, heterogeneous material lying on top of bedrock: includes soil, unweathered fragments of parent rock and rock fragments weathered from bedrock. [178]
- **Salar (aka Playa):** the flat floor of a closed basin in an arid region, usually rich in evaporite minerals such as sodium carbonate, sodium borate and other unusual salts. [178] Salar is the spanish word for salt.
- **Soil:** the surface accumulation of sand, clay and humus that composes the regolith, but excluding the larger fragments of unweathered rock. [178]

Appendix C: McMurdo Dry Valleys Soil

This appendix lists the soil samples analyzed from the McMurdo Dry Valleys (MDV) of Antarctica in Chapters 2 and 3. A total of 44 soil samples and 17 permafrost samples were collected from 11 different pits (Pits 1, 2, 3, 4, 7, 8, 9, 10, 11, 13, and 20) located within 5 different valleys: Taylor, Wright, Victoria, Beacon and University. Tables are separated by valley and pit and listed in order of increasing elevation. The information in each table includes each sample's soil identification number, depth of the horizon from which the sample was taken (in cm), depth used when plotting soil profiles (in cm), and sample type either soil or permafrost.

Taylor Valley Pit #1 (Elevation: 21 ± 5.5 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|------------|
| ANTV0701 | 0-1 | 0 | Soil |
| ANTV0702 | 1-8 | 4 | Soil |
| ANTV0703 | 8-28 | 18 | Soil |
| ANTV0705 | 26-28 | 27 | Soil |
| ANTV0704 | 28+ | 28 | Permafrost |

Taylor Valley Pit #2 (Elevation: 21 ± 5.5 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|------------|
| ANTV0706 | 0-1 | 0 | Soil |
| ANTV0707 | 1-9 | 5 | Soil |
| ANTV0708 | 9-12 | 11 | Soil |
| ANTV0709 | 12-17 | 15 | Soil |
| ANTV0710 | 17-20 | 18 | Soil |
| ANTV0711 | 20-24 | 22 | Soil |
| ANTV0712 | 24-28 | 26 | Soil |
| ANTV0713 | 28+ | 28 | Permafrost |

Taylor Valley Pit #4 (Elevation: 41 ± 4.9 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|------------|
| ANTV0721 | 1-7 | 3 | Soil |
| ANTV0722 | 7-26 | 17 | Soil |
| ANTV0723 | 26-29 | 27 | Soil |
| ANTV0724 | 29+ | 29 | Permafrost |

Taylor Valley Pit #3 (Elevation: 108 ± 5.5 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|------------|
| ANTV0714 | 0-1 | 0 | Soil |
| ANTV0715 | 1-8 | 4 | Soil |
| ANTV0716 | 8-18 | 13 | Soil |
| ANTV0717 | 18-34 | 26 | Soil |
| ANTV0719 | 32-34 | 33 | Soil |
| ANTV0718 | 34+ | 34 | Permafrost |

Wright Valley Pit #13 (Elevation: 182 ± 5.9 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|------------|
| ANWV0755 | 1-8 | 4 | Soil |
| ANWV0756 | 8-23 | 15 | Soil |
| ANWV0757 | 23+ | 23 | Permafrost |

Victoria Valley Pit #8 (Elevation: 357 ± 5.8 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|------------|
| ANVV0731 | 1-7 | 3 | Soil |
| ANVV0732 | 7-13 | 10 | Soil |
| ANVV0733 | 13-19 | 16 | Soil |
| ANVV0734 | 19+ | 19 | Permafrost |

Victoria Valley Pit #9 (Elevation: 394 ± 5.2 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|------------|
| ANVV0736 | 1-2 | 2 | Soil |
| ANVV0737 | 2-14 | 8 | Soil |
| ANVV0738 | 14-27 | 21 | Soil |
| ANVV0739 | 27+ | 27 | Permafrost |

Beacon Valley Pit #11 (Elevation: 1209 ± 6.4 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|-----------|
| ANBV0744 | 0-1 | 0 | Soil |
| ANBV0745 | 1-7 | 2 | Soil |
| ANBV0746 | 7-105+ | 25 | Soil |
| ANBV0747 | 7-105+ | 50 | Soil |
| ANBV0748 | 7-105+ | 75 | Soil |

Beacon Valley Pit #20 (Elevation: 1240 ± 5.6 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|------------|
| ANBV07SK01 | 0-1 | 0 | Soil |
| ANBV07SK02L | 1-3 | 2 | Soil |
| ANBV07SK03L | 3-10 | 7 | Soil |
| ANBV07SK04 | 10-15 | 12 | Soil |
| ANBV07SK05 | 18-20 | 19 | Soil |
| ANBV07SK05 #4 | 20.0-20.3 | 20.2 | Permafrost |
| ANBV07SK05 #5 | 20.3-20.5 | 20.4 | Permafrost |
| ANBV07SK05 #6 | 20.5-20.7 | 20.6 | Permafrost |
| ANBV07SK05 #7 | 20.7-20.9 | 20.8 | Permafrost |
| ANBV07SK05 #8 | 21.9-21.1 | 21.0 | Permafrost |
| ANBV07SK05 #9 | 21.1-21.3 | 21.2 | Permafrost |
| ANBV07SK05 #10 | 21.3-21.5 | 21.4 | Permafrost |
| ANBV07SK05 #11 | 21.5-21.7 | 21.6 | Permafrost |

University Valley Pit #7 (Elevation: 1683 ± 5.9 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|------------|
| ANUV0725 | 0-1 | 0 | Soil |
| ANUV0726 | 1-9 | 5 | Soil |
| ANUV0727 | 9-20 | 15 | Soil |
| ANUV0728 | 20-34 | 25 | Soil |
| ANUV0729 | 34+ | 34 | Permafrost |

University Valley Pit #10 (Elevation: 1703 ± 5.5 m)

| Soil Identification | Soil Horizon Depth (cm) | Soil Profile Depth (cm) | Soil Type |
|---------------------|-------------------------|-------------------------|------------|
| ANUV0740 | 0-1 | 0 | Soil |
| ANUV0741 | 1-10 | 5 | Soil |
| ANUV0742 | 10-19 | 15 | Soil |
| ANUV0743 | 19+ | 19 | Permafrost |

Appendix D: Concentration of Soluble Ions in the Soils from the McMurdo Dry Valleys by Ion Chromatography and Acid-Base Titration

This appendix provides data tables for all 11 pits in the McMurdo Dry Valleys discussed in Chapters 2 and 3. These tables include the concentration of solution ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , NO_3^- , ClO_4^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-}) present in each soil horizon in each pit and the total ion concentration of each ion within the entire pit as measured by ion chromatography (IC) and acid-base titration. The procedure for the IC and acid-base titration analyses is discussed in Chapters 2 and 3. The concentrations are given in two ways: the amount in the soil leachate solution (in μM) and the amount in the soil (in mg/kg or $\mu\text{g}/\text{kg}$). The volume of the soil leachate solution was 5 mL for ClO_4^- , 10 mL for HCO_3^- and CO_3^{2-} and 25 mL for all other ions.

Not detected (N.D.) is listed if the concentration was below the instrument's limit of detection. If the ion was not present in any samples from within a pit it was excluded from the table. The limits of detection for the soil leachate solution are, 0.01 μM for all ions (and their equivalent values in $\mu\text{g}/\text{kg}$ or mg/kg for the soil) except for ClO_4^- which is 0.05 μ for the soil leachate solution (or 25 $\mu\text{g}/\text{kg}$ for the soil). The permafrost samples in Pit 20 were not analyzed for ClO_4^- therefore not analyzed (N.A.) is listed.

The standard deviation for these measurements are, $\leq\pm 35\%$ for Na^+ and ClO_4^- , $\leq\pm 40\%$ for SO_4^{2-} , $\leq\pm 45\%$ for K^+ , Mg^{2+} , CO_3^{2-} and PO_4^{3-} , $\leq\pm 50\%$ for NH_4^+ , Ca^{2+} , Cl^- and NO_3^- , and $\leq\pm 200\%$ for HCO_3^- , unless otherwise indicated.

Taylor Valley Pit #1 Ion Concentrations in the Soil Leachate Solution^{a*}

| Sample Identification | Na ⁺ (μM) | NH ₄ ⁺ (μM) | K ⁺ (μM) | Mg ²⁺ (μM) | Ca ²⁺ (μM) | Cl ⁻ (μM) | NO ₃ ⁻ (μM) | SO ₄ ²⁻ (μM) | PO ₄ ³⁻ (μM) | ClO ₄ ⁻ (μM) | HCO ₃ ⁻ (μM) | CO ₃ ²⁻ (μM) |
|-----------------------|----------------------|-----------------------------------|---------------------|-----------------------|-----------------------|----------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| ANTV0701 | 417 | 3 | 138 | 36 | 388 | 15 | 3 | 389 | 0.83 | 0.22 | 0.47 | 0.07 |
| ANTV0702 | 2934 | 18 | 181 | 10 | 28 | 737 | 65 | 94 | 17.14 | 0.18 | 0.87 | 1.09 |
| ANTV0703 | 450 | 1 | 36 | 1 | 3 | 240 | 9 | 6 | 19.88 | 0.09 | 0.35 | N.D. |
| ANTV0705 | 446 | 1 | 27 | 2 | 8 | 10 | 1 | 28 | 22.33 | N.D. | 0.40 | 0.01 |
| ANTV0704 | 532 | 2 | 47 | N.D. | 3 | 48 | 1 | 4 | 6.87 | N.D. | 0.34 | 0.13 |
| Total | 4779 | 24 | 428 | 50 | 430 | 1049 | 80 | 521 | 67.06 | 0.50 | 2.44 | 1.30 |

Taylor Valley Pit #1 Ion Concentrations in the Soil^{a*}

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (μg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (μg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | PO ₄ ³⁻ (mg/kg) | ClO ₄ ⁻ (μg/kg) | HCO ₃ ⁻ (μg/kg) | CO ₃ ²⁻ (μg/kg) |
|-----------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| ANTV0701 | 240 | 1137 | 135 | 21829 | 388 | 13 | 4 | 934 | 2 | 109 | 724 | 108 |
| ANTV0702 | 1686 | 7953 | 177 | 6126 | 28 | 653 | 101 | 226 | 41 | 92 | 1327 | 1634 |
| ANTV0703 | 258 | 548 | 35 | 843 | 4 | 212 | 14 | 13 | 47 | 47 | 536 | N.D. |
| ANTV0705 | 256 | 452 | 26 | 1300 | 8 | 9 | 2 | 68 | 53 | N.D. | 614 | 15 |
| ANTV0704 | 306 | 787 | 46 | N.D. | 3 | 42 | 2 | 10 | 16 | N.D. | 521 | 200 |
| Total | 2746 | 10878 | 418 | 30097 | 430 | 930 | 123 | 1251 | 159 | 248 | 3721 | 1957 |

^a Ba²⁺ was also present at 0.42 μM in the soil leachate solution (or 1440 μg/kg in the soil) in sample ANTV0701.

* The standard deviation of 3 ions was higher than indicated above: NH₄⁺ in ANTV0701 (55%), PO₄³⁻ in ANTV0701 (173%) and CO₃²⁻ in ANTV0705 (173%).

Taylor Valley Pit #2 Ion Concentrations in the Soil Leachate Solution *

| Sample Identification | Na ⁺ (μM) | NH ₄ ⁺ (μM) | K ⁺ (μM) | Mg ²⁺ (μM) | Ca ²⁺ (μM) | Cl ⁻ (μM) | NO ₃ ⁻ (μM) | SO ₄ ²⁻ (μM) | PO ₄ ³⁻ (μM) | ClO ₄ ⁻ (μM) | HCO ₃ ⁻ (μM) | CO ₃ ²⁻ (μM) |
|-----------------------|----------------------|-----------------------------------|---------------------|-----------------------|-----------------------|----------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| ANTV0706 | 638 | 3 | 85 | 21 | 129 | 121 | 8 | 173 | 3.36 | N.D. | 0.36 | 0.09 |
| ANTV0707 | 2095 | 13 | 124 | 23 | 63 | 988 | 46 | 205 | 7.42 | N.D. | 0.45 | 0.25 |
| ANTV0708 | 1701 | 7 | 117 | 41 | 70 | 1113 | 72 | 93 | 5.46 | N.D. | 0.36 | 0.27 |
| ANTV0709 | 3516 | 15 | 156 | 22 | 13 | 3456 | 231 | 57 | 11.11 | 2.22 | 0.51 | 0.09 |
| ANTV0710 | 1867 | 7 | 72 | 2 | 3 | 1468 | 52 | 19 | 40.18 | N.D. | 0.39 | 0.07 |
| ANTV0711 | 927 | 3 | 41 | N.D. | 2 | 304 | 11 | 9 | 45.06 | N.D. | 0.34 | 0.08 |
| ANTV0712 | 1580 | 7 | 101 | 6 | 23 | 18 | N.D. | 56 | 16.00 | N.D. | 1.44 | 0.21 |
| ANTV0713 | 2052 | 10 | 177 | 13 | 28 | 894 | 23 | 114 | 21.70 | 0.57 | 1.01 | 0.17 |
| Total | 14376 | 64 | 873 | 128 | 331 | 8362 | 442 | 726 | 150.27 | 2.79 | 4.87 | 1.23 |

Taylor Valley Pit #2 Ion Concentrations in the Soil *

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (μg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (μg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | PO ₄ ³⁻ (mg/kg) | ClO ₄ ⁻ (μg/kg) | HCO ₃ ⁻ (μg/kg) | CO ₃ ²⁻ (μg/kg) |
|-----------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| ANTV0706 | 366 | 1482 | 83 | 12749 | 129 | 107 | 12 | 416 | 8 | N.D. | 553 | 138 |
| ANTV0707 | 1204 | 5767 | 122 | 13694 | 63 | 875 | 71 | 492 | 18 | N.D. | 692 | 368 |
| ANTV0708 | 977 | 3011 | 114 | 25040 | 70 | 986 | 112 | 224 | 13 | N.D. | 553 | 400 |
| ANTV0709 | 2020 | 6842 | 152 | 13278 | 13 | 3062 | 358 | 136 | 26 | 1103 | 770 | 138 |
| ANTV0710 | 1073 | 3083 | 70 | 1473 | 3 | 1302 | 80 | 45 | 95 | N.D. | 598 | 107 |
| ANTV0711 | 533 | 1297 | 40 | N.D. | 2 | 269 | 16 | 22 | 107 | N.D. | 521 | 123 |
| ANTV0712 | 908 | 3223 | 99 | 3760 | 23 | 16 | N.D. | 135 | 38 | N.D. | 2195 | 308 |
| ANTV0713 | 1179 | 4320 | 173 | 7655 | 28 | 792 | 35 | 274 | 52 | 286 | 1539 | 262 |
| Total | 8261 | 29024 | 853 | 77649 | 332 | 7410 | 685 | 1744 | 357 | 1389 | 7421 | 1844 |

* The standard deviation of 1 ion was higher than indicated above: ClO₄⁻ in ANTV0713 (60%).

Taylor Valley Pit #4 Ion Concentrations in the Soil Leachate Solution*

| Sample Identification | Na ⁺ (μ M) | NH ₄ ⁺ (μ M) | K ⁺ (μ M) | Mg ²⁺ (μ M) | Ca ²⁺ (μ M) | Cl ⁻ (μ M) | NO ₃ ⁻ (μ M) | SO ₄ ²⁻ (μ M) | PO ₄ ³⁻ (μ M) | HCO ₃ ⁻ (μ M) | CO ₃ ²⁻ (μ M) |
|-----------------------|-------------------------------|--|------------------------------|--------------------------------|--------------------------------|-------------------------------|--|---|---|---|---|
| ANTV0721 | 1737 | 20 | 136 | 22 | 33 | 999 | 49 | 48 | 6.24 | 0.56 | 0.29 |
| ANTV0722 | 968 | 31 | 87 | 26 | 48 | 406 | 16 | 29 | 6.51 | 0.38 | 0.08 |
| ANTV0723 | 741 | 3 | 86 | 9 | 12 | 23 | 1 | 7 | 15.43 | 0.71 | 0.04 |
| ANTV0724 | 567 | N.D. | 33 | 2 | 4 | 34 | 1 | 6 | 38.86 | 0.31 | N.D. |
| Total | 4013 | 54 | 342 | 59 | 96 | 1462 | 67 | 90 | 67.04 | 1.96 | 0.41 |

Taylor Valley Pit #4 Ion Concentrations in the Soil*

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | PO ₄ ³⁻ (mg/kg) | HCO ₃ ⁻ (μ g/kg) | CO ₃ ²⁻ (μ g/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|----------------------------|---|--|--|--|--|
| ANTV0721 | 992 | 9 | 132 | 13 | 33 | 880 | 75 | 114 | 15 | 856 | 430 |
| ANTV0722 | 554 | 14 | 85 | 16 | 48 | 359 | 25 | 69 | 15 | 579 | 123 |
| ANTV0723 | 426 | 1 | 84 | 5 | 12 | 21 | 2 | 17 | 37 | 1077 | 61 |
| ANTV0724 | 324 | N.D. | 32 | 1 | 4 | 30 | 1 | 14 | 92 | 469 | N.D. |
| Total | 2296 | 24 | 333 | 36 | 96 | 1289 | 104 | 214 | 159 | 2980 | 615 |

* The standard deviation of 1 ion was higher than indicated above: NH₄⁺ in ANTV0722 (57%).

Taylor Valley Pit #3 Ion Concentrations in the Soil Leachate Solution*

| Sample Identification | Na ⁺ (μM) | NH ₄ ⁺ (μM) | K ⁺ (μM) | Mg ²⁺ (μM) | Ca ²⁺ (μM) | Cl ⁻ (μM) | NO ₃ ⁻ (μM) | SO ₄ ²⁻ (μM) | PO ₄ ³⁻ (μM) | ClO ₄ ⁻ (μM) | HCO ₃ ⁻ (μM) | CO ₃ ²⁻ (μM) |
|-----------------------|----------------------|-----------------------------------|---------------------|-----------------------|-----------------------|----------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| ANTV0714 | 511 | 10 | 83 | 23 | 146 | 116 | 6 | 67 | 0.46 | N.D. | 0.40 | 0.18 |
| ANTV0715 | 2188 | 27 | 109 | 88 | 126 | 1279 | 55 | 103 | 0.67 | 0.10 | 0.41 | 0.21 |
| ANTV0716 | 895 | 14 | 63 | 7 | 126 | 383 | 16 | 15 | 0.88 | N.D. | 0.41 | 0.03 |
| ANTV0717 | 588 | 14 | 40 | 2 | 4 | 18 | 2 | 4 | 3.32 | N.D. | 0.64 | N.D. |
| ANTV0719 | 543 | 10 | 49 | 15 | 15 | 29 | 3 | 4 | 1.99 | N.D. | 0.78 | N.D. |
| ANTV0718 | 645 | 13 | 56 | 9 | 11 | 17 | 1 | 3 | 3.03 | N.D. | 0.58 | N.D. |
| Total | 5371 | 88 | 401 | 144 | 427 | 1841 | 82 | 195 | 10.34 | 0.10 | 3.22 | 0.42 |

Taylor Valley Pit #3 Ion Concentrations in the Soil*

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | PO ₄ ³⁻ (μg/kg) | ClO ₄ ⁻ (μg/kg) | HCO ₃ ⁻ (μg/kg) | CO ₃ ²⁻ (μg/kg) |
|-----------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| ANTV0714 | 293 | 4 | 81 | 14 | 146 | 103 | 9 | 161 | 1081 | N.D. | 609 | 276 |
| ANTV0715 | 1257 | 12 | 106 | 53 | 126 | 1133 | 85 | 246 | 1582 | 52 | 629 | 307 |
| ANTV0716 | 513 | 6 | 62 | 4 | 125 | 338 | 24 | 35 | 2076 | N.D. | 629 | 46 |
| ANTV0717 | 339 | 6 | 39 | 1 | 4 | 16 | 2 | 8 | 7910 | N.D. | 974 | N.D. |
| ANTV0719 | 312 | 5 | 48 | 9 | 15 | 25 | 4 | 10 | 4708 | N.D. | 1191 | N.D. |
| ANTV0718 | 370 | 6 | 55 | 5 | 11 | 15 | 2 | 8 | 7186 | N.D. | 880 | N.D. |
| Total | 3084 | 40 | 391 | 88 | 427 | 1630 | 127 | 469 | 24543 | 52 | 4911 | 629 |

* The standard deviation of 2 ions was higher than indicated above: ClO₄⁻ in ANTV0715 (173%) and PO₄³⁻ in ANTV0715 (58%).

Wright Valley Pit #13 Ion Concentrations in the Soil Leachate Solution*

| Sample Identification | Na ⁺ (μM) | NH ₄ ⁺ (μM) | K ⁺ (μM) | Mg ²⁺ (μM) | Ca ²⁺ (μM) | Cl ⁻ (μM) | NO ₃ ⁻ (μM) | SO ₄ ²⁻ (μM) | PO ₄ ³⁻ (μM) | HCO ₃ ⁻ (μM) | CO ₃ ²⁻ (μM) |
|-----------------------|----------------------|-----------------------------------|---------------------|-----------------------|-----------------------|----------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| ANWV0755 | 667 | 9 | 48 | 108 | 163 | 546 | 85 | 98 | 0.67 | 0.24 | 0.06 |
| ANWV0756 | 321 | 4 | 25 | 10 | 14 | 53 | 5 | 12 | 0.63 | 0.01 | N.D. |
| ANWV0757 | 262 | N.D. | 29 | 11 | 13 | 17 | 3 | 7 | 0.54 | N.D. | N.D. |
| Total | 1250 | 12 | 103 | 129 | 190 | 616 | 93 | 117 | 1.84 | 0.25 | 0.06 |

Wright Valley Pit #13 Ion Concentrations in the Soil*

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | PO ₄ ³⁻ (μg/kg) | HCO ₃ ⁻ (μg/kg) | CO ₃ ²⁻ (μg/kg) |
|-----------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| ANWV0755 | 383 | 4 | 47 | 66 | 163 | 484 | 132 | 234 | 1583 | 366 | 92 |
| ANWV0756 | 185 | 2 | 25 | 6 | 14 | 47 | 7 | 30 | 1491 | 22 | N.D. |
| ANWV0757 | 151 | N.D. | 29 | 7 | 14 | 15 | 5 | 17 | 1289 | N.D. | N.D. |
| Total | 718 | 6 | 100 | 78 | 190 | 546 | 144 | 281 | 4363 | 388 | 92 |

* The standard deviation of 5 ions was higher than indicated above: Mg²⁺ in ANWV0756 (51%), Ca²⁺ in ANWV0756 (51%) and ANWV0757 (50%), NO₃⁻ in ANWV0757 (77%) and HCO₃⁻ in ANWV0757 (628%).

Victoria Valley Pit #8 Ion Concentrations in the Soil Leachate Solution*

| Sample Identification | Na ⁺ (μ M) | NH ₄ ⁺ (μ M) | K ⁺ (μ M) | Mg ²⁺ (μ M) | Ca ²⁺ (μ M) | Cl ⁻ (μ M) | NO ₃ ⁻ (μ M) | SO ₄ ²⁻ (μ M) | PO ₄ ³⁻ (μ M) | HCO ₃ ⁻ (μ M) | CO ₃ ²⁻ (μ M) |
|-----------------------|-------------------------------|--|------------------------------|--------------------------------|--------------------------------|-------------------------------|--|---|---|---|---|
| ANVV0731 | 323 | 5 | 45 | 15 | 127 | 34 | 3 | 49 | 1.13 | 0.29 | 0.07 |
| ANVV0732 | 674 | 18 | 49 | 45 | 735 | 175 | 39 | 874 | 1.45 | 0.19 | N.D. |
| ANVV0733 | 583 | 11 | 44 | 20 | 125 | 134 | 20 | 162 | 0.66 | 0.21 | 0.08 |
| ANVV0734 | 626 | N.D. | 43 | 27 | 147 | 148 | 25 | 255 | 0.98 | 0.40 | N.D. |
| Total | 2206 | 34 | 181 | 106 | 1134 | 490 | 88 | 1341 | 4.22 | 1.09 | 0.15 |

Victoria Valley Pit #8 Ion Concentrations in the Soil*

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | PO ₄ ³⁻ (mg/kg) | HCO ₃ ⁻ (μ g/kg) | CO ₃ ²⁻ (μ g/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|----------------------------|---|--|--|--|--|
| ANVV0731 | 185 | 2 | 44 | 9 | 127 | 30 | 5 | 117 | 3 | 444 | 108 |
| ANVV0732 | 388 | 8 | 48 | 27 | 737 | 155 | 60 | 2100 | 3 | 287 | N.D. |
| ANVV0733 | 334 | 5 | 43 | 12 | 125 | 118 | 31 | 389 | 2 | 318 | 123 |
| ANVV0734 | 360 | N.D. | 42 | 16 | 148 | 131 | 39 | 614 | 2 | 615 | N.D. |
| Total | 1267 | 15 | 177 | 65 | 1136 | 434 | 136 | 3220 | 10 | 1664 | 230 |

* The standard deviation of 3 ions was higher than indicated above: NH₄⁺ (56%), Cl⁻ (61%), and NO₃⁻ (101%) all in ANVV0732.

Victoria Valley Pit #9 Ion Concentrations in the Soil Leachate Solution*

| Sample Identification | Na ⁺ (μM) | NH ₄ ⁺ (μM) | K ⁺ (μM) | Mg ²⁺ (μM) | Ca ²⁺ (μM) | Cl ⁻ (μM) | NO ₃ ⁻ (μM) | SO ₄ ²⁻ (μM) | ClO ₄ ⁻ (μM) | HCO ₃ ⁻ (μM) | CO ₃ ²⁻ (μM) |
|-----------------------|----------------------|-----------------------------------|---------------------|-----------------------|-----------------------|----------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| ANVV0736 | 1950 | 34 | 64 | 201 | 1478 | 1916 | 234 | 1769 | N.D. | 0.33 | N.D. |
| ANVV0737 | 1447 | 24 | 65 | 304 | 1336 | 1592 | 476 | 990 | 0.12 | 0.34 | N.D. |
| ANVV0738 | 770 | 7 | 44 | 58 | 206 | 440 | 89 | 111 | N.D. | 0.25 | 0.07 |
| ANVV0739 | 721 | 8 | 47 | 38 | 143 | 343 | 76 | 39 | N.D. | 0.19 | 0.12 |
| Total | 4888 | 73 | 221 | 601 | 3163 | 4292 | 876 | 2909 | 0.12 | 1.11 | 0.19 |

Victoria Valley Pit #9 Ion Concentrations in the Soil*

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | ClO ₄ ⁻ (μg/kg) | HCO ₃ ⁻ (μg/kg) | CO ₃ ²⁻ (μg/kg) |
|-----------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| ANVV0736 | 1118 | 15 | 63 | 122 | 1478 | 1695 | 363 | 4240 | N.D. | 505 | N.D. |
| ANVV0737 | 832 | 11 | 64 | 185 | 1339 | 1411 | 738 | 2377 | 62 | 521 | N.D. |
| ANVV0738 | 443 | 3 | 43 | 35 | 207 | 390 | 139 | 268 | N.D. | 381 | 107 |
| ANVV0739 | 415 | 4 | 46 | 23 | 143 | 305 | 118 | 94 | N.D. | 288 | 185 |
| Total | 2807 | 33 | 216 | 365 | 3167 | 3801 | 1357 | 6979 | 62 | 1695 | 292 |

* The standard deviation of 1 ion was higher than indicated above: NH₄⁺ (58%) in ANVV0739.

Beacon Valley Pit #11 Ion Concentrations in the Soil Leachate Solution*

| Sample Identification | Na ⁺ (μM) | NH ₄ ⁺ (μM) | K ⁺ (μM) | Mg ²⁺ (μM) | Ca ²⁺ (μM) | Cl ⁻ (μM) | NO ₃ ⁻ (μM) | SO ₄ ²⁻ (μM) | ClO ₄ ⁻ (μM) | HCO ₃ ⁻ (μM) |
|-----------------------|----------------------|-----------------------------------|---------------------|-----------------------|-----------------------|----------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|
| ANBV0745 | 2428 | 74 | 58 | 723 | 5066 | 2128 | 2824 | 9166 | 1.16 | 0.22 |
| ANBV0746 | 976 | 36 | 26 | 146 | 144 | 1218 | 1146 | 679 | 0.74 | 0.17 |
| ANBV0747 | 775 | 26 | 22 | 26 | 38 | 954 | 459 | 258 | 0.37 | 0.05 |
| ANBV0748 | 648 | 23 | 26 | 12 | 34 | 873 | 467 | 335 | 0.34 | 0.07 |
| Total | 4826 | 159 | 133 | 908 | 5282 | 5173 | 4895 | 10437 | 2.60 | 0.51 |

Beacon Valley Pit #11 Ion Concentrations in the Soil*

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | ClO ₄ ⁻ (μg/kg) | HCO ₃ ⁻ (μg/kg) |
|-----------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| ANBV0745 | 1395 | 33 | 57 | 439 | 5074 | 1886 | 4377 | 22006 | 575 | 334 |
| ANBV0746 | 560 | 16 | 26 | 89 | 144 | 1079 | 1775 | 1629 | 370 | 256 |
| ANBV0747 | 445 | 12 | 22 | 16 | 38 | 846 | 711 | 619 | 183 | 83 |
| ANBV0748 | 372 | 11 | 26 | 8 | 35 | 774 | 724 | 805 | 167 | 99 |
| Total | 2774 | 72 | 130 | 551 | 5291 | 4585 | 7587 | 25059 | 1294 | 772 |

* The standard deviation of 6 ions was higher than indicated above: Na⁺ in ANBV0747 (42%) and ANBV0748 (53%), NH₄⁺ (97%) in ANBV0748, K⁺ in ANBV0748 (55%), Mg²⁺ in ANBV0747 (63%), and Cl⁻ in ANBV0746 (78%).

Beacon Valley Pit #20 Ion Concentrations in the Soil Leachate Solution*

| Sample Identification | Na ⁺ (μ M) | NH ₄ ⁺ (μ M) | K ⁺ (μ M) | Mg ²⁺ (μ M) | Ca ²⁺ (μ M) | Cl ⁻ (μ M) | NO ₃ ⁻ (μ M) | SO ₄ ²⁻ (μ M) | PO ₄ ³⁻ (μ M) | ClO ₄ ⁻ (μ M) | HCO ₃ ⁻ (μ M) |
|-----------------------|-------------------------------|--|------------------------------|--------------------------------|--------------------------------|-------------------------------|--|---|---|---|---|
| ANBV07SK01 | 1348 | 223 | 156 | 216 | 935 | 2084 | 508 | 884 | N.D. | 0.20 | 0.03 |
| ANBV07SK02 | 2762 | 227 | 134 | 606 | 4477 | 3024 | 1285 | 4031 | N.D. | 0.48 | 0.03 |
| ANBV07SK03 | 2649 | 240 | 133 | 412 | 3802 | 2532 | 1158 | 3222 | N.D. | 0.57 | 0.02 |
| ANBV07SK04 | 1508 | 259 | 134 | 80 | 963 | 1734 | 401 | 1047 | N.D. | 0.09 | 0.02 |
| ANBV07SK05 | 1935 | 267 | 200 | 101 | 1498 | 1439 | 355 | 1417 | N.D. | 0.09 | 0.03 |
| Total | 10202 | 1216 | 756 | 1416 | 11675 | 10813 | 3707 | 10602 | N.D. | 1.43 | 0.15 |
| ANBV07SK#4 | 806 | 8 | 16 | 37 | 212 | 373 | 221 | 428 | 0.09 | N.A. | N.D. |
| ANBV07SK#5 | 543 | 12 | 10 | 31 | 72 | 288 | 76 | 240 | 0.27 | N.A. | 0.01 |
| ANBV07SK#6 | 668 | 26 | 11 | 38 | 91 | 272 | 120 | 284 | 0.09 | N.A. | 0.05 |
| ANBV07SK#7 | 583 | 21 | 7 | 5 | 18 | 215 | 88 | 148 | 0.59 | N.A. | 0.05 |
| ANBV07SK#8 | 498 | 18 | 8 | 6 | 15 | 231 | 76 | 134 | 0.66 | N.A. | 0.03 |
| ANBV07SK#9 | 485 | 20 | 7 | 3 | 13 | 220 | 85 | 109 | 0.74 | N.A. | 0.07 |
| ANBV07SK#10 | 526 | 20 | 8 | 4 | 17 | 233 | 82 | 121 | 0.68 | N.A. | 0.07 |
| ANBV07SK#11 | 500 | 21 | 5 | 0.5 | 10 | 304 | 79 | 73 | 1 | N.A. | N.D. |

* The standard deviation of 11 ions was higher than indicated above: K⁺ in ANBV07SK02 (60%), ANBV07SK04 (97%) and ANBV07SK05 (97%), Mg²⁺ in ANBV07SK04 (59%) and ANBV07SK05 (64%), and Cl⁻ in ANBV07SK01 (73%), NO₃⁻ in ANBV07SK05 (58%), and PO₄³⁻ in ANBV07SK#4 (173%) and ANBV07SK#6 (173%) and HCO₃⁻ in ANBV07SK03 (229%) and ANBV07SK#4 (352%).

Beacon Valley Pit #20 Ion Concentrations in the Soil*

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | PO ₄ ³⁻ (μg/kg) | ClO ₄ ⁻ (μg/kg) | HCO ₃ ⁻ (μg/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|----------------------------|---|--|--|--|--|
| ANBV07SK01 | 809 | 101 | 153 | 131 | 936 | 1848 | 788 | 2123 | N.D. | 100 | 53 |
| ANBV07SK02 | 1657 | 102 | 131 | 368 | 4485 | 2680 | 1993 | 9681 | N.D. | 237 | 53 |
| ANBV07SK03 | 1589 | 108 | 130 | 250 | 3809 | 2244 | 1795 | 7738 | N.D. | 283 | 37 |
| ANBV07SK04 | 904 | 117 | 131 | 49 | 965 | 1537 | 621 | 2514 | N.D. | 44 | 37 |
| ANBV07SK05 | 1161 | 120 | 195 | 62 | 1501 | 1275 | 551 | 3404 | N.D. | 44 | 53 |
| Total | 6119 | 548 | 739 | 860 | 11697 | 9584 | 5747 | 25461 | N.D. | 709 | 233 |
| ANBV07SK#4 | 483 | 4 | 16 | 23 | 213 | 331 | 342 | 1028 | N.D. | N.A. | N.D. |
| ANBV07SK#5 | 326 | 5 | 9 | 19 | 72 | 256 | 118 | 577 | 632 | N.A. | 22 |
| ANBV07SK#6 | 401 | 12 | 11 | 23 | 91 | 241 | 186 | 681 | 211 | N.A. | 69 |
| ANBV07SK#7 | 350 | 10 | 7 | 3 | 18 | 191 | 136 | 355 | 1397 | N.A. | 83 |
| ANBV07SK#8 | 299 | 8 | 7 | 3 | 15 | 204 | 119 | 322 | 1569 | N.A. | 52 |
| ANBV07SK#9 | 291 | 9 | 7 | 2 | 13 | 195 | 131 | 262 | 1767 | N.A. | 99 |
| ANBV07SK#10 | 315 | 9 | 7 | 3 | 17 | 207 | 127 | 291 | 1621 | N.A. | 99 |
| ANBV07SK#11 | 300 | 10 | 5 | 0.3 | 10 | 270 | 123 | 175 | 1997 | N.A. | 99 |

* The standard deviation of 11 ions was higher than indicated above: K⁺ in ANBV07SK02 (60%), ANBV07SK04 (97%) and ANBV07SK05 (97%), Mg²⁺ in ANBV07SK04 (59%) and ANBV07SK05 (64%), and Cl⁻ in ANBV07SK01 (73%), NO₃⁻ in ANBV07SK05 (58%), and PO₄³⁻ in ANBV07SK#4 (173%) and ANBV07SK#6 (173%) and HCO₃⁻ in ANBV07SK03 (229%) and ANBV07SK#4 (352%).

University Valley Pit #7 Ion Concentrations in the Soil Leachate Solution

| Sample Identification | Na ⁺ (μ M) | NH ₄ ⁺ (μ M) | K ⁺ (μ M) | Mg ²⁺ (μ M) | Ca ²⁺ (μ M) | Ba ²⁺ (μ M) | Cl ⁻ (μ M) | NO ₃ ⁻ (μ M) | SO ₄ ²⁻ (μ M) | ClO ₄ ⁻ (μ M) | HCO ₃ ⁻ (μ M) |
|-----------------------|-------------------------------|--|------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|--|---|---|---|
| ANUV0725 | 1714 | 7 | 79 | 822 | 2197 | 10 | 328 | 1638 | 1823 | 0.33 | 0.16 |
| ANUV0726 | 2247 | 8 | 115 | 1968 | 3315 | 10 | 1121 | 2896 | 2969 | 1.27 | 0.22 |
| ANUV0727 | 2049 | 9 | 94 | 1071 | 457 | N.D. | 598 | 1876 | 586 | 0.49 | 0.12 |
| ANUV0728 | 1652 | 5 | 81 | 778 | 715 | N.D. | 324 | 807 | 830 | 0.26 | 0.10 |
| ANUV0729 | 1982 | 10 | 116 | 731 | 3454 | 12 | 283 | 656 | 3177 | 0.20 | 0.08 |
| Total | 9644 | 39 | 485 | 5371 | 10138 | 32 | 2655 | 7873 | 9384 | 2.55 | 0.67 |

University Valley Pit #7 Ion Concentrations in the Soil

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Ba ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | ClO ₄ ⁻ (μ g/kg) | HCO ₃ ⁻ (μ g/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|---|--|--|--|
| ANUV0725 | 985 | 3 | 77 | 500 | 2201 | 35 | 291 | 2540 | 4378 | 166 | 240 |
| ANUV0726 | 1291 | 4 | 113 | 1195 | 3321 | 34 | 994 | 4488 | 7128 | 630 | 334 |
| ANUV0727 | 1177 | 4 | 92 | 651 | 457 | N.D. | 530 | 2907 | 1406 | 244 | 178 |
| ANUV0728 | 949 | 2 | 79 | 473 | 716 | N.D. | 288 | 1251 | 1993 | 128 | 146 |
| ANUV0729 | 1139 | 4 | 113 | 444 | 3461 | 41 | 251 | 1017 | 7631 | 100 | 116 |
| Total | 5542 | 18 | 474 | 3263 | 10157 | 111 | 2353 | 12203 | 22535 | 1268 | 1014 |

University Valley Pit #10 Ion Concentrations in the Soil Leachate Solution*

| Sample Identification | Na ⁺ (μ M) | NH ₄ ⁺ (μ M) | K ⁺ (μ M) | Mg ²⁺ (μ M) | Ca ²⁺ (μ M) | Ba ²⁺ (μ M) | Cl ⁻ (μ M) | NO ₃ ⁻ (μ M) | SO ₄ ²⁻ (μ M) | ClO ₄ ⁻ (μ M) | HCO ₃ ⁻ (μ M) |
|-----------------------|-------------------------------|--|------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|--|---|---|---|
| ANUV0740 | 970 | 110 | 47 | 355 | 1631 | 70 | 191 | 647 | 1351 | 0.13 | 0.09 |
| ANUV0741 | 1696 | 128 | 60 | 965 | 2305 | 64 | 242 | 1383 | 2241 | 0.18 | 0.10 |
| ANUV0742 | 1667 | 158 | 56 | 843 | 2540 | 107 | 254 | 1192 | 2417 | 0.16 | 0.06 |
| ANUV0743 | 919 | 170 | 35 | 210 | 460 | 1 | 186 | 448 | 518 | 0.06 | 0.05 |
| Total | 5252 | 567 | 198 | 2373 | 6937 | 242 | 874 | 3670 | 6527 | 0.53 | 0.28 |

University Valley Pit #10 Ion Concentrations in the Soil*

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Ba ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | ClO ₄ ⁻ (μ g/kg) | HCO ₃ ⁻ (μ g/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|---|--|--|--|
| ANUV0740 | 557 | 50 | 46 | 215 | 1633 | 168 | 169 | 1002 | 3241 | 63 | 131 |
| ANUV0741 | 975 | 58 | 59 | 586 | 2311 | 154 | 215 | 2145 | 5384 | 91 | 147 |
| ANUV0742 | 958 | 71 | 55 | 512 | 2544 | 268 | 225 | 1847 | 5803 | 78 | 84 |
| ANUV0743 | 529 | 77 | 34 | 128 | 462 | 3 | 165 | 695 | 1245 | 31 | 69 |
| Total | 3019 | 256 | 193 | 1442 | 6950 | 593 | 775 | 5689 | 15673 | 262 | 431 |

* The standard deviation of 1 ion was higher than indicated above: NO₃⁻ in ANUV0741 (86%).

Appendix E: Concentration of Soluble Ions in the Soils from the McMurdo Dry Valleys by the Ion Selective Electrodes in WCL

This appendix provides data tables for Taylor Valley Pits 1 and 2 and University Valley Pits 7 and 10 in the McMurdo Dry Valleys discussed in Chapter 2. These tables include the concentration of soluble ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , and NO_3^-) present in each soil horizon in each pit and the total ion concentration of each ion within the entire pit as measured by the ion selective electrodes (ISE) in the Wet Chemistry Laboratory (WCL) testbeds. The procedure for the analysis of these soils by WCL is discussed in Chapter 2. The concentrations are given in two ways: the amount in the 25 mL of soil leachate solution (in μM) and the amount in the soil (in mg/kg).

Not detected (N.D.) is listed if the concentration was below the instrument's limit of detection. The limits of detection for the soil leachate solution are, 0.1 μM for +1 ions, 0.4 μM for +2 ions, 0.9 μM for Cl^- , and 10.0 μM for NO_3^- (and their equivalent values in mg/kg for the soil).

The standard deviations for these measurements are based upon the average instrument noise for each sensor. The standard deviation for the concentrations of ions in the soil leachate solutions are, $\pm 5.1 \mu\text{M}$ for Na^+ and K^+ , $\pm 7.9 \mu\text{M}$ for NH_4^+ , $\pm 11.0 \mu\text{M}$ for Mg^{2+} and Ca^{2+} , $\pm 17.9 \mu\text{M}$ for Ba^{2+} , $\pm 25.3 \mu\text{M}$ for Cl^- , and 0.29 mM for NO_3^- (and their equivalent values in mg/kg in the soil) unless otherwise indicated.

Note: Calculations were performed which indicate the concentration of ClO_4^- present in some of these soils samples, as determined by ion chromatography, was not present at high enough levels to interfere with the response of the NO_3^- ISE.

Taylor Valley Pit #1 Ion Concentration in Soil Leachate Solution

| Sample Identification | Na ⁺ (μM) | NH ₄ ⁺ (μM) | K ⁺ (μM) | Mg ²⁺ (μM) | Ca ²⁺ (μM) | Ba ²⁺ (μM) | Cl ⁻ (μM) | NO ₃ ⁻ (μM) |
|-----------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|
| ANTV0701 | 2.13 | 2.05 | 13.47 | 22.60 | 65.14 | 0.42 | 0.98 | 11.00 |
| ANTV0702 | 8.37 | 4.25 | 20.63 | N.D. | N.D. | N.D. | 28.17 | 71.78 |
| ANTV0703 | 6.50 | 1.56 | 10.05 | N.D. | N.D. | N.D. | 3.58 | N.D. |
| ANTV0705 | 4.85 | 1.16 | 9.16 | N.D. | N.D. | N.D. | N.D. | N.D. |
| ANTV0704 | 2.40 | 0.15 | 4.53 | N.D. | 2.52 | N.D. | 2.11 | N.D. |
| Total | 24.25 | 9.16 | 57.84 | 22.60 | 67.66 | 0.42 | 34.84 | 82.78 |

Taylor Valley Pit #1 Ion Concentration in Soil

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Ba ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|---|
| ANTV0701 | 1.22 | 0.92 | 13.16 | 13.73 | 65.27 | 1.44 | 0.87 | 17.05 |
| ANTV0702 | 4.81 | 1.91 | 20.16 | N.D. | N.D. | N.D. | 24.96 | 111.27 |
| ANTV0703 | 3.74 | 0.70 | 9.83 | N.D. | N.D. | N.D. | 3.17 | N.D. |
| ANTV0705 | 2.79 | 0.52 | 8.95 | N.D. | N.D. | N.D. | N.D. | N.D. |
| ANTV0704 | 1.38 | 0.07 | 4.43 | N.D. | 2.52 | N.D. | 1.87 | N.D. |
| Total | 13.94 | 4.13 | 56.53 | 13.73 | 67.79 | 1.44 | 30.88 | 128.32 |

Taylor Valley Pit #2 Ion Concentration in Soil Leachate Solution

| Sample Identification | Na ⁺ (μ M) | NH ₄ ⁺ (μ M) | K ⁺ (μ M) | Mg ²⁺ (μ M) | Ca ²⁺ (μ M) | Cl ⁻ (μ M) | NO ₃ ⁻ (μ M) |
|-----------------------|-------------------------------|--|------------------------------|--------------------------------|--------------------------------|-------------------------------|--|
| ANTV0706 | 23.02 | 14.26 | 61.90 | 77.32 | 185.43 | 69.31 | 176.25 |
| ANTV0707 | 137.33 | 9.17 | 106.62 | 9.92 | 36.60 | 515.74 | 415.98 |
| ANTV0708 | 50.50 | 25.07 | 97.47 | 34.87 | 77.16 | 574.68 | 437.18 |
| ANTV0709 | 282.50 | 19.15 | 165.33 | N.D. | N.D. | 1506.10 | 432.71 |
| ANTV0710 | 158.65 | 13.04 | 118.23 | N.D. | N.D. | 372.43 | N.D. |
| ANTV0711 | 73.82 | 1.89 | 56.40 | N.D. | N.D. | 67.29 | N.D. |
| ANTV0712 | 274.56 | 18.52 | 191.04 | N.D. | 21.51 | N.D. | N.D. |
| ANTV0713 | 112.97 | 35.72 | 245.64 | 3.00 | 21.11 | 250.95 | 15.51 |
| Total | 1113.34 | 136.83 | 1042.64 | 125.10 | 341.82 | 3356.51 | 1477.63 |

Taylor Valley Pit #2 Ion Concentration in Soil

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|----------------------------|---|
| ANTV0706 | 13.23 | 6.43 | 60.51 | 46.98 | 185.80 | 61.43 | 273.21 |
| ANTV0707 | 78.93 | 4.14 | 104.22 | 6.03 | 36.68 | 457.12 | 644.81 |
| ANTV0708 | 29.03 | 11.31 | 95.27 | 21.19 | 77.31 | 509.35 | 677.68 |
| ANTV0709 | 162.36 | 8.64 | 161.60 | N.D. | N.D. | 1334.89 | 670.75 |
| ANTV0710 | 91.18 | 5.88 | 115.57 | N.D. | N.D. | 330.10 | N.D. |
| ANTV0711 | 42.43 | 0.85 | 55.13 | N.D. | N.D. | 59.64 | N.D. |
| ANTV0712 | 157.80 | 8.35 | 186.74 | N.D. | 21.56 | N.D. | N.D. |
| ANTV0713 | 64.93 | 16.11 | 240.10 | 1.82 | 21.15 | 222.42 | 24.05 |
| Total | 639.88 | 61.71 | 1019.13 | 76.02 | 342.49 | 2974.95 | 2290.51 |

University Valley Pit #7 Ion Concentration in Soil Leachate Solution

| Sample Identification | Na ⁺ (μ M) | NH ₄ ⁺ (μ M) | K ⁺ (μ M) | Mg ²⁺ (μ M) | Ca ²⁺ (μ M) | Ba ²⁺ (μ M) | Cl ⁻ (μ M) | NO ₃ ⁻ (μ M) |
|-----------------------|-------------------------------|--|------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|--|
| ANUV0725 | 7.64 | 1.13 | 5.58 | 151.52 | 349.91 | 10.33 | 35.25 | 118.09 |
| ANUV0726 | 7.02 | 2.62 | 8.28 | 134.64 | 212.89 | 9.83 | 84.66 | 188.07 |
| ANUV0727 | 10.22 | 0.81 | 6.82 | 33.93 | 40.73 | N.D. | 51.09 | 132.16 |
| ANUV0728 | 5.35 | N.D. | 4.22 | 22.81 | 36.78 | N.D. | 30.29 | 51.71 |
| ANUV0729 | 11.26 | 1.78 | 8.77 | 173.00 | 375.76 | 12.07 | 25.89 | 28.52 |
| Total | 41.49 | 6.35 | 33.67 | 515.91 | 1016.08 | 32.23 | 227.18 | 518.54 |

University Valley Pit #7 Ion Concentration in Soil

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Ba ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|---|
| ANUV0725 | 4.39 | 0.51 | 5.45 | 92.07 | 350.60 | 35.47 | 31.24 | 183.05 |
| ANUV0726 | 4.04 | 1.18 | 8.09 | 81.81 | 213.31 | 33.74 | 75.04 | 291.52 |
| ANUV0727 | 5.87 | 0.37 | 6.67 | 20.62 | 40.81 | N.D. | 45.28 | 204.87 |
| ANUV0728 | 3.07 | N.D. | 4.12 | 13.86 | 36.85 | N.D. | 26.85 | 80.15 |
| ANUV0729 | 6.47 | 0.80 | 8.57 | 105.12 | 376.50 | 41.45 | 22.95 | 44.20 |
| Total | 23.84 | 2.86 | 32.91 | 313.48 | 1018.06 | 110.65 | 201.36 | 803.81 |

University Valley Pit #10 Ion Concentration in Soil Leachate Solution

| Sample Identification | Na ⁺ (μ M) | NH ₄ ⁺ (μ M) | K ⁺ (μ M) | Mg ²⁺ (μ M) | Ca ²⁺ (μ M) | Ba ²⁺ (μ M) | Cl ⁻ (μ M) | NO ₃ ⁻ (μ M) |
|-----------------------|-------------------------------|--|------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|--|
| ANUV0740 | 884.60 | 12.40 | 69.30 | 894.30 | 1980.60 | 69.70 | 115.10 | 602.80 |
| ANUV0741 | 865.04 | 11.69 | 68.96 | 820.57 | 1933.62 | 64.25 | 120.12 | 645.20 |
| ANUV0742 | 1631.50 | 20.36 | 88.79 | 1410.34 | 2377.72 | 107.10 | 162.93 | 2487.37 |
| ANUV0743 | 727.50 | 12.24 | 40.01 | 228.02 | 606.84 | 1.36 | 115.68 | 399.11 |
| Total | 4108.64 | 56.69 | 267.05 | 3353.23 | 6898.78 | 242.41 | 513.83 | 4134.48 |

University Valley Pit #10 Ion Concentration in Soil

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Ba ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|---|
| ANUV0740 | 356.99 | 3.93 | 47.56 | 381.55 | 1393.39 | 168.02 | 71.63 | 656.10 |
| ANUV0741 | 346.87 | 3.68 | 47.03 | 5014.56 | 1351.70 | 153.91 | 74.28 | 697.79 |
| ANUV0742 | 683.35 | 6.69 | 63.25 | 624.51 | 1736.16 | 267.95 | 105.24 | 2809.89 |
| ANUV0743 | 304.76 | 55.52 | 28.50 | 100.99 | 443.17 | 3.41 | 74.73 | 450.93 |
| Total | 1691.97 | 69.82 | 186.34 | 6121.61 | 4924.41 | 593.28 | 325.88 | 4614.70 |

Appendix F: Atacama Desert Soil

This appendix lists the soil samples analyzed from the Atacama Desert in Chile in Chapter 4. A total of 56 soil samples were collected from three different locations (AT10 OE, AT10 6 and AT10 P) located within the Desert. At these locations either a pit was dug (AT10 OE and AT10 6) or a linear transect of soil was collected from the top 5 cm (AT10 P). Tables are separated by location. The approximate locations can be seen on the map of the Atacama (Chapter 4, Figure 33). The information in each pit table includes each sample's soil identification number, and the approximate depth at which the sample was collected. The table for the linear transect includes each sample's soil identification and the distance the sample was collected from the start of the transect.

Atacama Pit AT10 OE

| Soil Identification | Depth (cm) |
|---------------------|------------|
| AT10 OE 0cm | 0 |
| AT10 OE 10cm | 10 |
| AT10 OE 20cm | 20 |
| AT10 OE 30cm | 30 |
| AT10 OE 40cm | 40 |
| AT10 OE 50cm | 50 |
| AT10 OE 60cm | 60 |
| AT10 OE 70cm | 70 |
| AT10 OE 80cm | 80 |
| AT10 OE 90cm | 90 |
| AT10 OE 100cm | 100 |
| AT10 OE 110cm | 110 |
| AT10 OE 120cm | 120 |
| AT10 OE 130cm | 130 |
| AT10 OE 140cm | 140 |
| AT10 OE 150cm | 150 |
| AT10 OE160cm | 160 |
| AT10 OE 170cm | 170 |
| AT10 OE 180cm | 180 |
| AT10 OE 190cm | 190 |
| AT10 OE 200cm | 200 |
| AT10 OE 210cm | 210 |
| AT10 OE 220cm | 220 |
| AT10 OE 230cm | 230 |
| AT10 OE 240cm | 240 |
| AT10 OE 250cm | 250 |

Atacama Pit AT10 6

| Soil Identification | Depth (cm) |
|---------------------|------------|
| AT10 6 0cm | 0 |
| AT10 6 15cm | 15 |
| AT10 6 30cm | 30 |
| AT10 6 45cm | 45 |
| AT10 6 60cm | 60 |
| AT10 6 75cm | 75 |
| AT10 6 95cm | 95 |
| AT10 6 110cm | 110 |
| AT10 6 125cm | 125 |
| AT10 6 140cm | 140 |
| AT10 6 155cm | 155 |
| AT10 6 170cm | 170 |

Atacama Linear Transect AT10 P

| Soil Identification | Distance from Start of Transect (m) |
|---------------------|-------------------------------------|
| AT10 P 21 | 0 |
| AT10 P 22 | 1 |
| AT10 P 23 | 2 |
| AT10 P 24 | 3 |
| AT10 P 25.0 | 4 |
| AT10 P 25.1 | 4.1 |
| AT10 P 25.2 | 4.2 |
| AT10 P 25.3 | 4.3 |
| AT10 P 25.4 | 4.4 |
| AT10 P 25.5 | 4.5 |
| AT10 P 25.6 | 4.6 |
| AT10 P 25.7 | 4.7 |
| AT10 P 25.8 | 4.8 |
| AT10 P 25.9 | 4.9 |
| AT10 P 26 | 5 |
| AT10 P 27 | 6 |
| AT10 P 28 | 7 |
| AT10 P 29 | 8 |

Appendix G: Concentration of Soluble Ions in the Soils from the Atacama Desert by Ion Chromatography and Acid-Base Titration

This appendix provides data tables for the three locations in the Atacama Desert discussed in Chapter 4. These tables include the concentration of solution ions (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , ClO_4^- , HCO_3^- , CO_3^{2-} , and SO_4^{2-}) present in each soil from each pit or linear transect and the total ion concentration of each ion within the entire pit (but not within the entire linear transect) as measured by ion chromatography (IC) and acid-base titration. The procedure for the IC and acid-base titration analyses is discussed in Chapter 4. The concentrations are given in two ways: the amount in the soil leachate solution (in $\mu\text{M}/\text{mM}$) and the amount in the soil (in mg/kg or $\mu\text{g}/\text{kg}$). The volume of the soil leachate solution was 10 mL for HCO_3^- and CO_3^{2-} and 5 mL for all other ions.

Not detected (N.D.) is listed if the concentration was below the instrument's limit of detection. The limits of detection for the soil leachate solution are, 0.01 μM for all ions (and their equivalent values in $\mu\text{g}/\text{kg}$ or mg/kg for the soil) except for ClO_4^- which is 0.05 μ for the soil leachate solution (or 25 $\mu\text{g}/\text{kg}$ for the soil).

The standard deviation for these measurements are, $\leq\pm 15\%$ for Na^+ , $\leq\pm 30\%$ for ClO_4^- , $\leq\pm 35\%$ for Li^+ , NH_4^+ , Mg^{2+} , and Cl^- , $\leq\pm 40\%$ for K^+ , Ca^{2+} , and $\leq\pm 50\%$ for NO_3^- , HCO_3^- , CO_3^{2-} , and SO_4^{2-} , unless otherwise indicated.

AT10 6 Ion Concentrations in the Soil Leachate Solution*

| Sample Depth | Na ⁺ (mM) | K ⁺ (mM) | Mg ²⁺ (mM) | Ca ²⁺ (mM) | Cl ⁻ (mM) | NO ₃ ⁻ (mM) | SO ₄ ²⁻ (mM) | ClO ₄ ⁻ (μM) | HCO ₃ ⁻ (μM) | CO ₃ ²⁻ (μM) |
|--------------|----------------------|---------------------|-----------------------|-----------------------|----------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| 0cm | 32.35 | 1.21 | N.D. | 10.03 | 8.78 | 0.14 | 99.06 | N.D. | 0.23 | N.D. |
| 15cm | 38.86 | 1.44 | N.D. | 16.85 | 2.53 | 0.30 | 126.92 | N.D. | 0.27 | N.D. |
| 30cm | 43.55 | 1.68 | N.D. | 17.69 | 10.99 | 0.06 | 171.51 | N.D. | 0.10 | N.D. |
| 45cm | 49.46 | 2.11 | N.D. | 18.35 | 11.90 | 1.87 | 165.24 | 0.46 | 0.25 | N.D. |
| 60cm | 112.41 | 3.63 | N.D. | 19.87 | 38.17 | 7.92 | 10.11 | 2.75 | 0.35 | N.D. |
| 75cm | 91.70 | 6.27 | N.D. | 11.94 | 13.07 | 9.88 | 84.95 | 6.44 | 0.53 | N.D. |
| 95cm | 129.63 | 4.72 | N.D. | 13.73 | 30.02 | 8.38 | 9.77 | 10.47 | 0.12 | 0.17 |
| 110cm | 460.17 | 5.47 | N.D. | 12.98 | 24.88 | 8.57 | 27.81 | 8.39 | 0.38 | 0.06 |
| 125cm | 442.48 | 9.99 | N.D. | 15.05 | 68.40 | 19.40 | 34.94 | 11.99 | 0.37 | 0.08 |
| 140cm | 234.26 | 5.66 | N.D. | 28.25 | 49.55 | 17.53 | 21.08 | 12.87 | 0.32 | 0.09 |
| 155cm | 1140.42 | 7.90 | N.D. | 18.24 | 18.92 | 3.47 | 56.61 | N.D. | 0.23 | N.D. |
| 170cm | 898.34 | 7.71 | 4.51 | 28.13 | 61.79 | 139.88 | 85.76 | 15.51 | 0.35 | 0.13 |
| Total | 3673.63 | 57.78 | 4.51 | 211.12 | 339.02 | 217.40 | 893.74 | 68.87 | 3.49 | 0.54 |

AT10 6 Ion Concentrations in the Soil*

| Sample Depth | Na ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | ClO ₄ ⁻ (μg/kg) | HCO ₃ ⁻ (μg/kg) | CO ₃ ²⁻ (μg/kg) |
|--------------|-------------------------|------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| 0cm | 3722 | 236 | N.D. | 2013 | 1559 | 45 | 47625 | N.D. | 137 | N.D. |
| 15cm | 4467 | 281 | N.D. | 3376 | 448 | 93 | 60962 | N.D. | 162 | N.D. |
| 30cm | 4997 | 327 | N.D. | 3538 | 1945 | 19 | 82214 | N.D. | 63 | N.D. |
| 45cm | 5674 | 411 | N.D. | 3669 | 2106 | 579 | 79210 | 229 | 150 | N.D. |
| 60cm | 12921 | 711 | N.D. | 3981 | 6767 | 2456 | 4856 | 1368 | 213 | N.D. |
| 75cm | 10530 | 1224 | N.D. | 2390 | 2314 | 3058 | 40762 | 3197 | 325 | N.D. |
| 95cm | 14886 | 921 | N.D. | 2749 | 5316 | 2594 | 4686 | 5199 | 75 | 104 |
| 110cm | 52843 | 1069 | N.D. | 2599 | 4407 | 2656 | 13342 | 4166 | 231 | 37 |
| 125cm | 50811 | 1951 | N.D. | 3014 | 12113 | 6008 | 16764 | 5958 | 225 | 49 |
| 140cm | 26928 | 1107 | N.D. | 5662 | 8784 | 5435 | 10123 | 6398 | 194 | 55 |
| 155cm | 131090 | 1545 | N.D. | 3656 | 3354 | 1075 | 27189 | N.D. | 138 | N.D. |
| 170cm | 103264 | 1507 | 548 | 5638 | 10953 | 43366 | 41193 | 7713 | 212 | 80 |
| Total | 422133 | 11290 | 548 | 42283 | 60066 | 67383 | 428926 | 34229 | 2125 | 326 |

* The standard deviation of 2 ions was over the amounts listed above: NO₃⁻ at 30 cm (90%) and CO₃²⁻ at 30 cm (81%).

AT10 OE Ion Concentrations in the Soil Leachate Solution*

| Sample Depth | Li ⁺ (mM) | Na ⁺ (mM) | NH ₄ ⁺ (mM) | K ⁺ (mM) | Mg ²⁺ (mM) | Ca ²⁺ (mM) | Cl ⁻ (mM) | NO ₃ ⁻ (mM) | SO ₄ ²⁻ (mM) | ClO ₄ ⁻ (μM) | HCO ₃ ⁻ (μM) | CO ₃ ²⁻ (μM) |
|--------------|----------------------|----------------------|-----------------------------------|---------------------|-----------------------|-----------------------|----------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| 0cm | 0.41 | 148.27 | 4.61 | 0.92 | 0.76 | 17.70 | 2.89 | 0.00 | 17.64 | 0.36 | 0.35 | N.D. |
| 10cm | 0.38 | 169.10 | 4.68 | 0.77 | 0.45 | 23.45 | 9.14 | 2.78 | 42.69 | 2.56 | 0.28 | N.D. |
| 20cm | 0.45 | 744.55 | 11.32 | 3.62 | 2.44 | 25.24 | 102.15 | 13.55 | 307.89 | 2.15 | 0.16 | 0.49 |
| 30cm | 0.72 | 812.94 | N.D. | 4.22 | 14.25 | 24.61 | 76.94 | 70.07 | 322.24 | 22.24 | 0.47 | 0.53 |
| 40cm | 0.59 | 645.94 | 6.56 | 10.68 | 17.30 | 40.40 | 40.94 | 41.26 | 181.23 | 47.20 | 0.32 | 0.84 |
| 50cm | 0.59 | 471.80 | 7.56 | 10.37 | 16.30 | 43.94 | 73.07 | 62.43 | 171.11 | 62.19 | 0.21 | 0.56 |
| 60cm | 0.58 | 527.86 | 12.41 | 15.24 | 21.95 | 35.17 | 129.30 | 124.76 | 47.43 | 60.21 | N.D. | 1.47 |
| 70cm | 0.47 | 307.99 | 7.49 | 19.83 | 19.56 | 21.01 | 88.14 | 90.84 | 57.20 | 75.67 | N.D. | 1.46 |
| 80cm | 0.56 | 282.25 | 8.84 | 7.85 | 17.34 | 25.06 | 56.86 | 54.62 | 58.31 | 51.73 | N.D. | 0.64 |
| 90cm | 1.37 | 798.51 | 96.70 | 13.07 | 0.18 | 1.04 | 21.06 | 28.31 | 18.90 | 22.41 | N.D. | 1.27 |
| 100cm | 1.27 | 698.19 | 135.42 | 17.62 | 5.37 | 12.36 | 33.42 | 50.31 | 36.11 | 24.53 | N.D. | 1.19 |
| 110cm | 1.35 | 971.65 | 18.94 | 22.36 | 8.49 | 9.57 | 159.27 | 66.11 | 42.88 | 87.83 | N.D. | 1.68 |
| 120cm | 1.41 | 958.43 | 107.44 | 14.71 | 3.37 | 4.46 | 111.28 | 63.23 | 27.28 | 68.23 | N.D. | 1.21 |
| 130cm | 1.15 | 766.41 | 17.88 | 9.36 | 1.01 | 2.40 | 67.54 | 53.08 | 21.85 | 45.60 | N.D. | 1.07 |
| 140cm | 1.24 | 791.88 | 42.34 | 13.36 | 0.38 | 1.97 | 38.11 | 82.41 | 32.49 | 97.67 | N.D. | 0.94 |
| 150cm | 0.99 | 933.14 | 324.66 | 19.83 | 0.60 | 25.77 | 45.11 | 77.63 | 122.72 | 122.03 | N.D. | 1.40 |
| 160cm | 0.86 | 825.20 | 139.76 | 17.03 | 0.23 | 9.47 | 44.44 | 52.34 | 77.12 | 59.34 | N.D. | 1.69 |
| 170cm | 1.17 | 777.20 | 17.95 | 14.76 | 0.42 | 8.93 | 41.56 | 46.56 | 86.28 | 65.74 | N.D. | 1.63 |
| 180cm | 1.67 | 927.62 | 23.79 | 9.48 | 0.10 | 2.77 | 47.69 | 44.85 | 62.75 | 40.68 | N.D. | 1.50 |
| 190cm | 0.80 | 598.30 | 19.60 | 9.17 | 0.04 | 0.80 | 13.54 | 65.05 | 47.66 | 46.76 | N.D. | 1.20 |
| 200cm | 1.28 | 724.91 | 30.44 | 7.75 | 0.04 | 0.76 | 10.70 | 61.21 | 26.50 | 21.52 | N.D. | 1.17 |
| 210cm | 1.11 | 743.04 | 267.12 | 9.51 | 0.05 | 1.09 | 7.65 | 19.38 | 16.41 | 26.42 | N.D. | 0.94 |
| 220cm | 0.72 | 602.12 | 24.73 | 7.92 | 0.05 | 1.20 | 18.17 | 53.44 | 48.75 | 18.78 | N.D. | 0.99 |
| 230cm | 0.59 | 588.56 | 13.30 | 8.61 | 0.08 | 1.92 | 14.05 | 50.66 | 68.14 | 14.39 | N.D. | 1.16 |
| 240cm | 1.21 | 804.21 | 34.17 | 9.34 | 0.06 | 1.70 | 16.23 | 47.93 | 59.31 | 11.55 | N.D. | 1.20 |
| 250cm | 1.36 | 854.21 | 35.57 | 11.64 | 0.08 | 2.21 | 15.70 | 48.14 | 100.98 | 13.70 | N.D. | 1.10 |
| Total | 24.31 | 17474.29 | 1413.28 | 289.01 | 130.90 | 344.99 | 1284.97 | 1370.96 | 2101.87 | 1111.49 | 1.78 | 27.33 |

* The standard deviation of 22 ions was over the amounts listed above: NH₄⁺ at 20 cm (49%) and 50 cm (43%), Mg²⁺ at 60 cm (44%), 130 cm (50%), 170 cm (41%) and 180 cm (58%), Ca²⁺ at 90 cm (41%), 150 cm (62%), 180 cm (62%) and 220 cm (49%), Cl⁻ at 40 cm (66%), 60 cm (62%), 160 cm (54%) and 210 cm (88%), NO₃⁻ at 40 cm (66%), 60 cm (63%), 160 cm (55%) and 210 cm (87%), and SO₄²⁻ at 0 cm (79%), 40 cm (63%), 160 cm (54%) and 210 cm (88%).

AT10 OE Ion Concentrations in the Soil*

| Sample Depth | Li ⁺ (mg/kg) | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | ClO ₄ ⁻ (μg/kg) | HCO ₃ ⁻ (μg/kg) | CO ₃ ²⁻ (μg/kg) |
|--------------|----------------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|----------------------------|---|--|--|--|--|
| 0cm | 14 | 17040 | 415 | 180 | 93 | 3545 | 512 | N.D. | 8469 | 181 | 212 | N.D. |
| 10cm | 13 | 19416 | 422 | 151 | 54 | 4694 | 1619 | 860 | 20482 | 1270 | 169 | N.D. |
| 20cm | 15 | 85466 | 1020 | 707 | 296 | 5052 | 18083 | 4195 | 147676 | 1069 | 100 | 295 |
| 30cm | 25 | 93343 | N.D. | 824 | 1729 | 4925 | 13624 | 21700 | 154607 | 11049 | 288 | 320 |
| 40cm | 20 | 74131 | 591 | 2084 | 2099 | 8082 | 7246 | 12773 | 86910 | 23432 | 194 | 504 |
| 50cm | 20 | 54216 | 682 | 2026 | 1981 | 8802 | 12949 | 19349 | 82160 | 30916 | 125 | 338 |
| 60cm | 20 | 60676 | 1120 | 2978 | 2668 | 7049 | 22920 | 38678 | 22781 | 29941 | N.D. | 879 |
| 70cm | 16 | 35428 | 676 | 3880 | 2378 | 4213 | 15635 | 28184 | 27492 | 37655 | N.D. | 874 |
| 80cm | 19 | 32418 | 797 | 1533 | 2105 | 5018 | 10072 | 16919 | 27984 | 25703 | N.D. | 381 |
| 90cm | 48 | 91798 | 8722 | 2555 | 21 | 208 | 3733 | 8779 | 9081 | 11143 | N.D. | 762 |
| 100cm | 44 | 80224 | 12209 | 3444 | 653 | 2476 | 5923 | 15592 | 17336 | 12192 | N.D. | 714 |
| 110cm | 47 | 111657 | 1708 | 4370 | 1032 | 1918 | 28225 | 20488 | 20588 | 43659 | N.D. | 1009 |
| 120cm | 49 | 110105 | 9685 | 2874 | 410 | 893 | 19715 | 19592 | 13095 | 33906 | N.D. | 725 |
| 130cm | 40 | 88124 | 1613 | 1830 | 123 | 481 | 11977 | 16460 | 10499 | 22679 | N.D. | 639 |
| 140cm | 43 | 90998 | 3817 | 2611 | 47 | 394 | 6754 | 25542 | 15600 | 48554 | N.D. | 565 |
| 150cm | 34 | 107242 | 29276 | 3876 | 73 | 5163 | 7994 | 24062 | 58930 | 60668 | N.D. | 842 |
| 160cm | 30 | 94894 | 12611 | 3331 | 28 | 1898 | 7881 | 16233 | 37058 | 29516 | N.D. | 1014 |
| 170cm | 40 | 89303 | 1618 | 2885 | 50 | 1788 | 7364 | 14428 | 41427 | 32676 | N.D. | 978 |
| 180cm | 58 | 106480 | 2143 | 1851 | 12 | 555 | 8441 | 13884 | 30098 | 20199 | N.D. | 898 |
| 190cm | 28 | 68774 | 1768 | 1793 | 5 | 161 | 2401 | 20168 | 22890 | 23254 | N.D. | 720 |
| 200cm | 44 | 83278 | 2744 | 1514 | 5 | 151 | 1895 | 18964 | 12721 | 10692 | N.D. | 701 |
| 210cm | 39 | 85378 | 24082 | 1858 | 6 | 219 | 1356 | 6007 | 7880 | 13133 | N.D. | 566 |
| 220cm | 25 | 69241 | 2232 | 1549 | 6 | 241 | 3222 | 16576 | 23425 | 9344 | N.D. | 596 |
| 230cm | 20 | 67539 | 1198 | 1680 | 10 | 383 | 2486 | 15679 | 32674 | 7142 | N.D. | 695 |
| 240cm | 42 | 92416 | 3081 | 1825 | 7 | 340 | 2876 | 14855 | 28477 | 5742 | N.D. | 719 |
| 250cm | 47 | 98034 | 3203 | 2272 | 10 | 443 | 2779 | 14901 | 48424 | 6800 | N.D. | 658 |
| Total | 843 | 2007619 | 127430 | 56479 | 15900 | 69093 | 227681 | 424869 | 1008766 | 552516 | 1088 | 16393 |

* The standard deviation of 22 ions was over the amounts listed above: NH₄⁺ at 20 cm (49%) and 50 cm (43%), Mg²⁺ at 60 cm (44%), 130 cm (50%), 170 cm (41%) and 180 cm (58%), Ca²⁺ at 90 cm (41%), 150 cm (62%), 180 cm (62%) and 220 cm (49%), Cl⁻ at 40 cm (66%), 60 cm (62%), 160 cm (54%) and 210 cm (88%), NO₃⁻ at 40 cm (66%), 60 cm (63%), 160 cm (87%), and SO₄²⁻ at 0 cm (79%), 40 cm (63%), 160 cm (54%) and 210 cm (88%).

AT10 P Ion Concentrations in the Soil Leachate Solution*

| Sample Identification | Li ⁺ (mM) | Na ⁺ (mM) | NH ₄ ⁺ (mM) | K ⁺ (mM) | Mg ²⁺ (mM) | Ca ²⁺ (mM) | Cl ⁻ (mM) | NO ₃ ⁻ (mM) | SO ₄ ²⁻ (mM) | ClO ₄ ⁻ (μM) | HCO ₃ ⁻ (μM) |
|-----------------------|----------------------|----------------------|-----------------------------------|---------------------|-----------------------|-----------------------|----------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|
| AT10 P 21 | 0.03 | 102.13 | 3.81 | 2.80 | 2.91 | 17.58 | 56.58 | 5.97 | 16.05 | 5.41 | 0.15 |
| AT10 P 22 | 0.03 | 57.32 | 2.44 | 1.98 | 0.59 | 12.51 | 11.37 | 1.52 | 11.27 | 0.79 | 0.12 |
| AT10 P 23 | 0.03 | 63.98 | 2.57 | 2.31 | 1.16 | 16.00 | 9.99 | 3.33 | 15.23 | 1.31 | 0.15 |
| AT10 P 24 | 0.01 | 42.80 | 2.88 | 1.57 | 0.46 | 13.44 | 9.02 | 1.58 | 11.52 | 0.67 | 0.16 |
| AT10 P 25 | 0.03 | 107.69 | 3.33 | 2.23 | 0.98 | 16.04 | 53.08 | 2.90 | 13.92 | 1.64 | 0.18 |
| AT10 P 25.1 | 0.03 | 80.98 | 1.22 | 2.09 | 0.70 | 18.31 | 34.81 | 2.19 | 16.74 | 0.77 | 0.15 |
| AT10 P 25.2 | 0.01 | 45.10 | 1.15 | 1.37 | 0.24 | 11.64 | 4.16 | 0.51 | 6.68 | 0.21 | 0.12 |
| AT10 P 25.3 | 0.01 | 64.77 | 1.00 | 1.75 | 0.51 | 13.93 | 26.92 | 1.28 | 11.69 | 0.77 | 0.17 |
| AT10 P 25.4 | 0.02 | 114.21 | 1.05 | 2.39 | 1.90 | 22.62 | 73.64 | 4.21 | 20.40 | 2.62 | 0.12 |
| AT10 P 25.5 | 0.03 | 84.18 | 1.31 | 3.17 | 0.76 | 13.60 | 32.33 | 2.54 | 12.46 | 1.44 | 0.12 |
| AT10 P 25.6 | 0.02 | 57.28 | 1.27 | 1.93 | 0.24 | 9.86 | 6.34 | 0.90 | 8.49 | 0.34 | 0.10 |
| AT10 P 25.7 | 0.02 | 45.49 | 1.19 | 2.06 | 0.20 | 12.18 | 3.79 | 0.53 | 10.40 | 0.17 | 0.12 |
| AT10 P 25.8 | 0.02 | 53.59 | 1.21 | 2.21 | 0.18 | 10.02 | 7.01 | 0.65 | 8.25 | 0.19 | 0.08 |
| AT10 P 25.9 | 0.03 | 62.73 | 1.36 | 1.43 | 0.47 | 10.69 | 8.72 | 1.25 | 8.92 | 0.61 | 0.10 |
| AT10 P 26 | 0.02 | 54.50 | 3.39 | 1.90 | 0.21 | 11.26 | 8.39 | 0.90 | 10.17 | 0.37 | 0.10 |
| AT10 P 27 | 0.02 | 49.97 | 3.16 | 1.61 | 0.12 | 8.36 | 2.71 | 0.41 | 6.74 | 0.14 | 0.11 |
| AT10 P 28 | 0.02 | 55.01 | 3.38 | 1.42 | 0.23 | 10.91 | 6.18 | 0.85 | 9.11 | 0.27 | 0.10 |
| AT10 P 29 | 0.01 | 71.15 | 3.79 | 2.32 | 3.47 | 21.50 | 39.75 | 7.30 | 18.07 | 4.94 | 0.16 |

* The standard deviation of 4 ions was over the amounts listed above: Cl⁻ at 25.2 (43%), NO₃⁻ at 25.2 (71%) and 27 (51%) and SO₄²⁻ at 25.2 (54%).

AT10 P Ion Concentrations in the Soil*

| Sample Identification | Li ⁺ (mg/kg) | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) | SO ₄ ²⁻ (mg/kg) | ClO ₄ ⁻ (μg/kg) | HCO ₃ ⁻ (μg/kg) |
|-----------------------|----------------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|----------------------------|---|--|--|--|
| AT10 P 21 | 1 | 11732 | 344 | 547 | 353 | 3520 | 10022 | 1849 | 7701 | 2687 | 94 |
| AT10 P 22 | 1 | 6581 | 220 | 386 | 71 | 2503 | 2013 | 471 | 5408 | 392 | 75 |
| AT10 P 23 | 1 | 7356 | 232 | 452 | 141 | 3207 | 1772 | 1033 | 7319 | 649 | 94 |
| AT10 P 24 | 1 | 4921 | 259 | 308 | 57 | 2695 | 1599 | 491 | 5533 | 335 | 98 |
| AT10 P 25 | 1 | 12378 | 301 | 436 | 119 | 3214 | 9408 | 900 | 6686 | 814 | 112 |
| AT10 P 25.1 | 1 | 9311 | 110 | 408 | 85 | 3669 | 6172 | 679 | 8043 | 384 | 89 |
| AT10 P 25.2 | 1 | 5185 | 104 | 268 | 29 | 2332 | 738 | 158 | 3208 | 104 | 75 |
| AT10 P 25.3 | 1 | 7450 | 90 | 342 | 62 | 2794 | 4774 | 397 | 5618 | 385 | 103 |
| AT10 P 25.4 | 1 | 13128 | 95 | 467 | 231 | 4534 | 13054 | 1304 | 9798 | 1305 | 75 |
| AT10 P 25.5 | 1 | 9676 | 118 | 619 | 93 | 2726 | 5731 | 788 | 5984 | 716 | 70 |
| AT10 P 25.6 | 1 | 6587 | 114 | 378 | 29 | 1976 | 1124 | 280 | 4079 | 170 | 61 |
| AT 10 P 25.7 | 1 | 5226 | 108 | 402 | 25 | 2439 | 671 | 166 | 4990 | 86 | 70 |
| AT10 P 25.8 | 1 | 6156 | 109 | 432 | 21 | 2006 | 1241 | 203 | 3962 | 95 | 52 |
| AT10 P 25.9 | 1 | 7210 | 123 | 279 | 57 | 2141 | 1546 | 386 | 4284 | 302 | 61 |
| AT10 P 26 | 1 | 6265 | 306 | 371 | 25 | 2257 | 1487 | 278 | 4887 | 182 | 61 |
| AT10 P 27 | 1 | 5745 | 285 | 315 | 15 | 1676 | 480 | 128 | 3238 | 71 | 66 |
| AT10 P 28 | 1 | 6325 | 305 | 278 | 28 | 2186 | 1095 | 265 | 4378 | 133 | 61 |
| AT10 P 29 | 1 | 8174 | 342 | 453 | 422 | 4307 | 7043 | 2263 | 8674 | 2455 | 98 |

* The standard deviation of 4 ions was over the amounts listed above: Cl⁻ at 25.2 (43%), NO₃⁻ at 25.2 (71%) and 27 (51%) and SO₄²⁻ at 25.2 (54%).

Appendix H: Concentration of Soluble Ions in the Soils from the Atacama Desert by the Ion Selective Electrodes in WCL

This appendix provides data tables for the three locations in the Atacama Desert discussed in Chapter 4. These tables include the concentration of soluble ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cl^- , and NO_3^-) present in five randomly selected soil samples from each location as measured by the ion selective electrodes (ISE) in the Wet Chemistry Laboratory (WCL) testbeds. The procedure for the analysis of these soils by WCL is discussed in Chapter 4. The concentrations are given in two ways: the amount in the 5 mL of soil leachate solution (in mM) and the amount in the soil (in mg/kg).

Not detected (N.D.) is listed if the concentration was below the instrument's limit of detection. The limits of detection for the soil leachate solution are, $0.1 \mu\text{M}$ for +1 ions, $0.4 \mu\text{M}$ for +2 ions, $0.9 \mu\text{M}$ for Cl^- , and $10.0 \mu\text{M}$ for NO_3^- (and their equivalent values in mg/kg for the soil).

The standard deviations for these measurements are based upon the average instrument noise for each sensor. The standard deviation for the concentrations of ions in the soil leachate solutions are, $\pm 5.1 \mu\text{M}$ for Na^+ and K^+ , $\pm 7.9 \mu\text{M}$ for NH_4^+ , $\pm 11.0 \mu\text{M}$ for Mg^{2+} and Ca^{2+} , $\pm 17.9 \mu\text{M}$ for Ba^{2+} , $\pm 25.3 \mu\text{M}$ for Cl^- , and 0.29 mM for NO_3^- (and their equivalent values in mg/kg in the soil) unless otherwise indicated.

Note: Calculations were performed which indicate the concentration of ClO_4^- present in some of these soils samples, as determined by ion chromatography (IC), were not present at high enough levels to interfere with the response of the NO_3^- ISE. However, the concentration of Li^+ seen in some of the soils, as determined by IC, was in some instances present at levels high enough to interfere with the response of the Li^+ ISE used as a reference (these soils have been marked with a †). In these instances, the mV response corresponding to the Li^+ concentration measured by the IC was calculated from the Nernst equation and subtracted from the Li^+ ISE response upon soil sample addition. Thus the Li^+ ISE response was corrected prior to calculating the concentration of the ions listed in these tables.

AT10 6 Ion Concentration in Soil Leachate Solution

| Sample Identification | Na ⁺ (mM) | NH ₄ ⁺ (mM) | K ⁺ (mM) | Mg ²⁺ (mM) | Ca ²⁺ (mM) | Ba ²⁺ (mM) | Cl ⁻ (mM) | NO ₃ ⁻ (mM) |
|-----------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|
| AT10 6 0cm | 0.01 | 0.00 | 0.05 | 0.35 | 1.45 | 0.03 | N.D. | N.D. |
| AT10 6 15cm | 0.02 | 0.00 | 0.02 | 2.51 | 8.89 | 0.30 | N.D. | N.D. |
| AT10 6 75cm | 2.07 | 0.12 | 0.70 | 0.06 | 0.95 | 0.04 | 2.29 | 2.90 |
| AT10 6 125cm | 15.43 | 0.26 | 0.73 | 0.80 | 2.01 | 0.23 | 8.37 | 5.70 |
| AT10 6 170cm | 38.06 | 0.36 | 0.28 | 0.49 | 0.19 | 0.39 | 21.32 | 49.31 |

AT10 6 Ion Concentration in Soil

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Ba ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|---|
| AT10 6 0cm | 5 | 1 | 36 | 151 | 1022 | 69 | N.D. | N.D. |
| AT10 6 15cm | 9 | 1 | 17 | 1165 | 6795 | 793 | N.D. | N.D. |
| AT10 6 75cm | 847 | 39 | 485 | 27 | 677 | 96 | 1445 | 3201 |
| AT10 6 125cm | 6383 | 85 | 511 | 352 | 1450 | 573 | 5343 | 6360 |
| AT10 6 170cm | 17601 | 130 | 221 | 237 | 154 | 1067 | 15201 | 61500 |

AT10 OE Ion Concentration in Soil Leachate Solution

| Sample Identification | Na ⁺ (mM) | NH ₄ ⁺ (mM) | K ⁺ (mM) | Mg ²⁺ (mM) | Ca ²⁺ (mM) | Ba ²⁺ (mM) | Cl ⁻ (mM) | NO ₃ ⁻ (mM) |
|-----------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|
| AT10 OE 0cm | 0.62 | 0.08 | 0.22 | 3.56 | 8.97 | 0.68 | N.D. | N.D. |
| AT10 OE 30cm | 123.92 | 0.43 | 0.71 | 3.47 | 6.56 | 1.25 | 6.93 | 6.85 |
| AT10 OE 120cm † | 97.59 | 0.97 | 4.29 | 5.01 | 6.93 | 0.85 | 6.51 | 5.94 |
| AT10 OE 180cm † | 54.18 | 1.23 | 5.29 | 2.02 | 3.70 | 0.88 | 1.47 | 2.00 |
| AT10 OE 240cm † | 18.42 | 0.62 | 1.93 | 0.34 | 0.53 | 0.11 | 1.29 | 3.99 |

AT10 OE Ion Concentration in Soil

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Ba ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|---|
| AT10 OE 0cm | 289 | 28 | 174 | 1753 | 7277 | 1891 | N.D. | N.D. |
| AT10 OE 30cm | 61136 | 167 | 594 | 1809 | 5640 | 3684 | 5274 | 9117 |
| AT10 OE 120cm † | 40949 | 318 | 3063 | 2221 | 5067 | 2131 | 4211 | 6724 |
| AT10 OE 180cm † | 22397 | 399 | 3720 | 883 | 2663 | 2173 | 937 | 2231 |
| AT10 OE 240cm † | 7149 | 188 | 1271 | 139 | 360 | 255 | 771 | 4172 |

AT10 P Ion Concentration in Soil Leachate Solution

| Sample Identification | Na ⁺ (mM) | NH ₄ ⁺ (mM) | K ⁺ (mM) | Mg ²⁺ (mM) | Ca ²⁺ (mM) | Ba ²⁺ (mM) | Cl ⁻ (mM) | NO ₃ ⁻ (mM) |
|-----------------------|-------------------------|--------------------------------------|------------------------|--------------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|
| AT10 P 21 | 5.92 | 0.12 | 0.27 | 1.02 | 1.42 | 0.21 | 6.20 | 0.79 |
| AT10 P 24 | 0.86 | 0.04 | 0.11 | 0.98 | 2.11 | 0.16 | 1.00 | 0.02 |
| AT10 P 25.4 | 8.97 | 0.09 | 0.25 | 1.30 | 2.92 | 0.22 | 7.03 | 0.37 |
| AT10 P 25.7 | 0.11 | 0.01 | 0.06 | 0.82 | 1.95 | 0.12 | 0.18 | N.D. |
| AT10 P 29 | 1.09 | 0.15 | 0.34 | 1.08 | 1.98 | 0.32 | 3.29 | 0.94 |

AT10 P Ion Concentration in Soil

| Sample Identification | Na ⁺ (mg/kg) | NH ₄ ⁺ (mg/kg) | K ⁺ (mg/kg) | Mg ²⁺ (mg/kg) | Ca ²⁺ (mg/kg) | Ba ²⁺ (mg/kg) | Cl ⁻ (mg/kg) | NO ₃ ⁻ (mg/kg) |
|-----------------------|----------------------------|---|---------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|---|
| AT10 P 21 | 2799 | 44 | 219 | 509 | 1166 | 593 | 4514 | 1001 |
| AT10 P 24 | 369 | 12 | 79 | 443 | 1576 | 410 | 663 | 24 |
| AT10 P 25.4 | 3796 | 30 | 180 | 583 | 2152 | 556 | 4584 | 421 |
| AT10 P 25.7 | 45 | 5 | 41 | 363 | 1426 | 301 | 118 | N.D. |
| AT10 P 29 | 532 | 57 | 283 | 557 | 1687 | 930 | 2483 | 1242 |

Appendix J: Comparison of the Geochemical Properties of the Soil from Three Extreme Environments: the north polar region of Mars, the McMurdo Dry Valleys of Antarctica and the Atacama Desert in Chile

This appendix provides information about all three extreme environments discussed in this work: Mars (Chapter 1), the McMurdo Dry Valleys (Chapters 2 and 3) and the Atacama Desert (Chapter 4). In particular this is a comparison of four locations within these environments: the Phoenix lander site in the north polar region of Mars, the coastal thaw zone and stable upland zone of the McMurdo Dry Valleys and the location of the linear transect, AT10 P, in the Atacama.

In each location, only the soil from the top 5 cm was compared. Figure 64 shows a comparison of the average pH measured in the soil leachate solutions from four locations. Figure 65 shows a comparison of the average electrical conductivity measured in the soil leachate solutions (with the EC of the Atacama solutions corrected to account for the difference in leaching ratio used). Figure 66 shows a comparison of the average concentration of soluble ions measured in the soil leachate solutions from four locations. Table 38 lists the geochemical properties of the soil from each of the four locations. Included are pH, electrical conductivity (EC), and individual ion concentrations, determined in from a solution of the soil leachate, as well as the ratio of the concentrations of the ionic species.

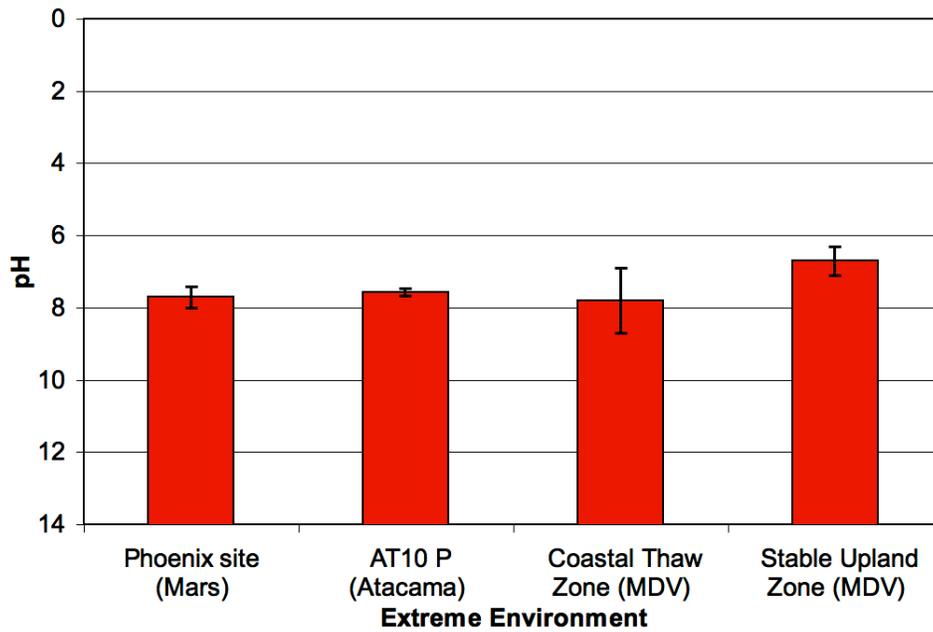


Figure 64: Comparison of the average pH measured in the soil leachates from four locations within three extreme environments: the Phoenix lander site on Mars, location AT10P in the Atacama Desert in Chile, and the coastal thaw zone and stable upland zone in the McMurdo Dry Valleys of Antarctica

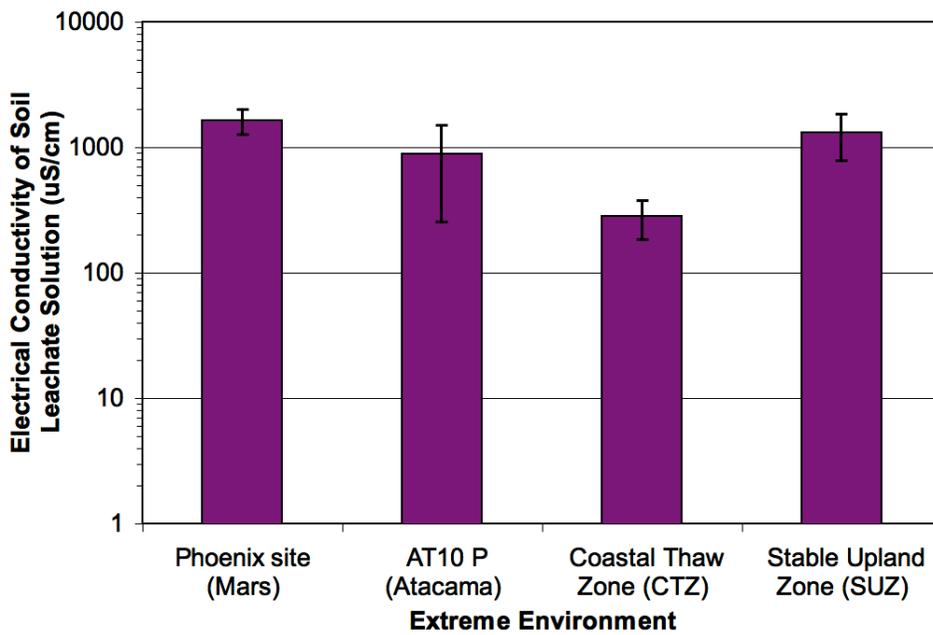


Figure 65: Comparison of the average electrical conductivity measured in the soil leachates from four locations within three extreme environments: the Phoenix lander site on Mars, location AT10P in the Atacama Desert in Chile, and the coastal thaw zone and stable upland zone in the McMurdo Dry Valleys of Antarctica

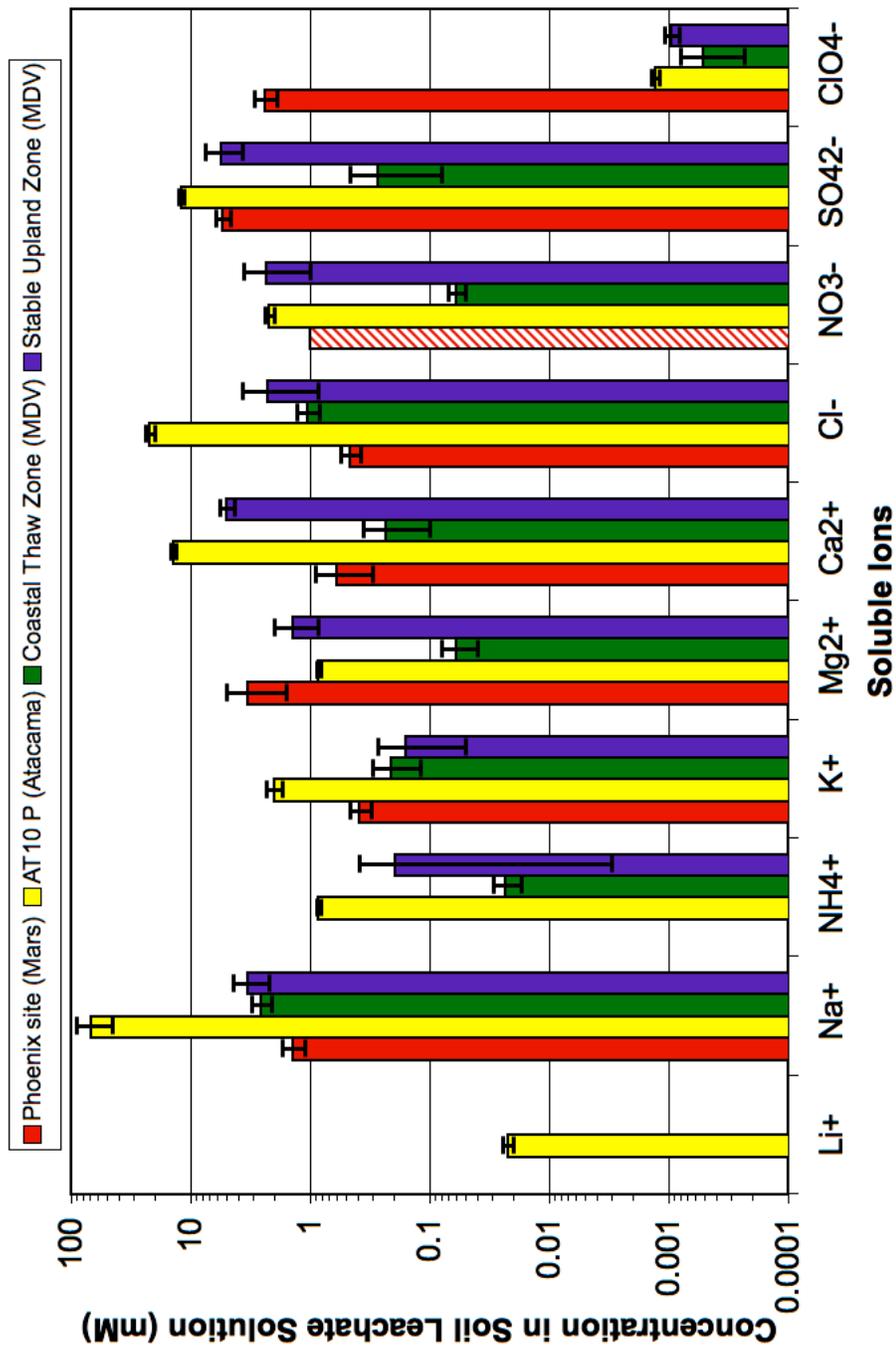


Figure 66: Comparison of the average concentration of soluble ions measured in the soil leachate solutions from four locations within three extreme environments: the Phoenix lander site on Mars, location AT10P in the Atacama Desert in Chile, and the coastal thaw zone and stable upland zone in the McMurdo Dry Valleys of Antarctica (The striped line for nitrate on Mars represents an estimate of the highest possible concentration in the soil leachate solution as determined from the measured conductivity.)

Table 38: Comparison of soils from the north polar region of Mars to soils from two extreme environments on Earth: AT10 P in the Atacama Desert, Chile and the stable upland zone of the McMurdo Dry Valleys, Antarctica. (All soils were collected at a depth of ≤ 5 cm.)

| Geochemical Property | Mars Phoenix Site ^a (n = 2) | Atacama AT10 P ^b (n = 18) | MDV CTZ ^c (n = 7) | MDV SUZ ^c (n = 7) |
|--|---|---|---------------------------------|---------------------------------|
| pH | 7.7 \pm 0.3 | 7.57 \pm 0.10 | 7.8 \pm 0.9 | 6.7 \pm 0.4 |
| EC (μ S/cm) | 1635 \pm 375 | 884 \pm 627 ^d | 283 \pm 97 | 1319 \pm 525 |
| Li ⁺ (mM) | N.D. ^e | 0.022 \pm 0.002 | N.D. ^e | N.D. ^e |
| Na ⁺ (mM) | 1.4 \pm 0.3 | 67.4 \pm 21.9 | 2.6 \pm 0.5 | 3.3 \pm 1.1 |
| NH ₄ ⁺ (mM) | N.D. ^e | 0.85 \pm 0.03 | 0.023 \pm 0.006 | 0.195 \pm 0.192 |
| K ⁺ (mM) | 0.39 \pm 0.08 | 2.0 \pm 0.3 | 0.21 \pm 0.09 | 0.16 \pm 0.11 |
| Mg ²⁺ (mM) | 3.3 \pm 1.7 | 0.85 \pm 0.03 | 0.06 \pm 0.02 | 1.41 \pm 0.56 |
| Ca ²⁺ (mM) | 0.6 \pm 0.3 | 13.9 \pm 0.8 | 0.23 \pm 0.13 | 4.98 \pm 0.68 |
| Cl ⁻ (mM) | 0.47 \pm 0.09 | 21.9 \pm 1.9 | 1.06 \pm 0.22 | 2.28 \pm 1.42 |
| NO ₃ ⁻ (mM) | N.D. ^e | 2.2 \pm 0.2 | 0.06 \pm 0.01 | 2.30 \pm 1.3 |
| SO ₄ ²⁻ (mM) | 5.4 \pm 0.78 | 12.0 \pm 0.6 | 0.27 \pm 0.19 | 5.62 \pm 1.93 |
| ClO ₄ ⁻ (μ M) | 2400 \pm 500 | 1.3 \pm 0.1 | 0.51 \pm 0.28 | 0.94 \pm 0.13 |
| [Na ⁺]:[K ⁺] | 2:1 to 6:1 | 20:1 to 53:1 | 7:1 to 26:1 | 8:1 to 88:1 |
| [Na ⁺]:[Mg ²⁺] | 1:1 to 6:1 | 52:1 to 146:1 | 6:1 to 31:1 | 0.4:1 to 1:1 |
| [Na ⁺]:[Ca ²⁺] | 1:1 to 5:1 | 3:1 to 7:1 | 0.01:1 to 0.04:1 | 0.2:1 to 0.9:1 |
| [Mg ²⁺]:[K ⁺] | 3:1 to 16:1 | 0.4:1 to 0.5:1 | 0.1:1 to 0.7:1 | 3:1 to 39:1 |
| [Mg ²⁺]:[Ca ²⁺] | 2:1 to 17:1 | 0.06:1 to 0.07:1 | 0.1:1 to 0.8:1 | 0.2:1 to 0.5:1 |
| [Mg ²⁺]:[Cl ⁻ +ClO ₄ ⁻] | 0.5:1 to 2:1 | 0.2:1 to 0.4:1 | 0.2:1 to 0.5:1 | 0.2:1 to 2:1 |
| [Ca ²⁺]:[K ⁺] | 0.6:1 to 3:1 | 6:1 to 9:1 | 0.3:1 to 3:1 | 16:1 to 113:1 |
| [Cl ⁻ +ClO ₄ ⁻]:[Na ⁺] | 1:1 to 3:1 | 0.2:1 to 0.5:1 | 0.3:1 to 0.6:1 | 0.2:1 to 2:1 |
| [Cl ⁻ +ClO ₄ ⁻]:[K ⁺] | 5:1 to 11:1 | 9:1 to 14:1 | 3:1 to 11:1 | 3:1 to 74:1 |
| [Cl ⁻ +ClO ₄ ⁻]:[Ca ²⁺] | 3:1 to 12:1 | 1:1 to 2:1 | 2:1 to 13:1 | 0.2:1 to 0.9:1 |
| [SO ₄ ²⁻]:[Na ⁺] | 3:1 to 6:1 | 0.1:1 to 0.3:1 | 0.03:1 to 0.2:1 | 0.8:1 to 3:1 |
| [SO ₄ ²⁻]:[K ⁺] | 10:1 to 20:1 | 5:1 to 7:1 | 0.3:1 to 4:1 | 14:1 to 51:1 |
| [SO ₄ ²⁻]:[Mg ²⁺] | 1:1 to 4:1 | 13:1 to 15:1 | 1:1 to 12:1 | 2:1 to 9:1 |
| [SO ₄ ²⁻]:[Ca ²⁺] | 5:1 to 21:1 | 0.8:1 to 1:1 | 0.2:1 to 5:1 | 0.7:1 to 2:1 |
| [SO ₄ ²⁻]:[Cl ⁻ +ClO ₄ ⁻] | 1:1 to 3:1 | 0.5:1 to 0.6:1 | 0.1:1 to 0.6:1 | 1:1 to 9:1 |

^a WCL ISE response (1 cm³ of soil assuming 1 g/cm³ was added to 25 mL of pure water)

^b IC of soil leachate solution (1 g of soil was leached in 5 mL of pure water for 1 hour)

^c IC of soil leachate solution (1 g of soil was leached in 25 mL of pure water for ~24 hours)

^d The conductivity of the Atacama soils was corrected to account for the difference in leaching ratios between the Atacama soil and the Martian soil.

^e N.D. = Not Detected. Value were below the instrument's limit of detection

References

- [1] L. Rothschild. Life in extreme environments: the universe may be more habitable than we thought. *Ad. Astra*, 14:32–40, 2002.
- [2] G. Certini, R. Scalenghe, and R. Admundson. A view of extraterrestrial soils. *European Journal of Soil Science*, 60:1078–1092, 2009.
- [3] L.K. Tamppari, R. Anderson, D. Archer, S. Douglas, S. Kouanves, C. McKay, D. Ming, Q. Moore, J. Quinn, P.H. Smith, **S. Stroble**, and A.P. Zent. Mcmurdo dry valleys, antarctica - a mars phoenix mission analog. In *41st Lunar and Planetary Science Conference*, 2010.
- [4] L.K. Tamppari, R.M. Anderson, P.D. Archer Jr., S. Douglas, S.P. Kounaves, C.P. McKay, D.W. Ming, Q. Moore, J.E. Quinn, P.H. Smith, **S. Stroble**, and A.P. Zent. Effects of extreme cold and aridity on soils and habitability: Mdv as an analog for the mars phoenix landing site. *Antarctic Science*, In Press.
- [5] S.P. Kounaves, M.H. Hecht, S.J. West, J.-M. Morookian, S.M.M. Young, R. Quinn, P. Grunthner, X. Wen, M. Weilert, C.A. Cable, A. Fisher, K. Gospodinova, J. Kapit, **S. Stroble**, P.-C. Hsu, B. Clark, D.W. Ming, and P.H. Smith. The meca wet chemistry laboratory on the 2007 phoenix mars scout lander. *Journal of Geophysical Research*, 114:E00A19, 2009.
- [6] S.P. Kounaves, M.H. Hecht, J. Kapit, K. Gospodinova, L. DeFlores, R.C. Quinn, W.V. Boynton, B.C. Clark, D.C. Catling, P. Hredzak, D.W. Ming, Q. Moore, J. Shusterman, **S. Stroble**, S.J. West, and S.M.M. Young. Wet chemistry experiments on the 2007 phoenix mars scout lander mission: Data analysis and results. *Journal of Geophysical Research*, 115:E00E10, 2010.
- [7] S.P. Kounaves, M.H. Hecht, J. Kapit, R.C. Quinn, Catling D.C, B.C. Clark, D.W. Ming, K. Gospodinova, P. Hredzak, K. McElhoney, and J. Shusterman. Soluble sulfate in the martian soil at the phoenix lander site. *Geophysical Research Letters*, 37:L09201, 2010.
- [8] S.S. Zumdahl. *Chemical Principles*. Houghton Mifflin, 6 edition, 2009. Table 4.1.
- [9] G. Horányi and I. Bakos. Experimental evidence demonstrating the occurrence of reduction processes of perchlorate ions in an acid medium at platinized platinum electrodes. *Journal of Electroanalytical Chemistry*, 331:727–737, 1992.
- [10] B.C. Clark, A.K. Baird, H.J. Rose Jr., K. Keil, A.J. Castro, W.C. Kelliher, C.D. Rowe, and P.H. Evans. Inorganic analyses of martian surface samples at the viking lander site. *Science*, 194:1283–1288, 1976.

- [11] G. Klingelhöfer, R.V. Morris, B. Bernhardt, C. Schröder, D.S. Rodionov, P.A. de Souza Jr., A. Yen, R. Gellert, E.N. Evlanov, B. Zubkov, J. Foh, U. Bonnes, E. Kankeleit, P. Gütlich, D.W. Ming, F. Renz, T. Wdowiak, S.W. Squyres, and R.E. Arvidson. Jarosite and hematite at meridiani planum from opportunity's mössbauer spectrometer. *Science*, 306:1740–1745, 2004.
- [12] S.W. Squyres, J.P. Grotzinger, R.E. Arvidson, J.F. Bell III, W. Calvin, P.R. Christensen, B.C. Clark, J.A. Crisp, W.H. Farrand, K.E. Herkenhoff, J.R. Johnson, G. Klingelhöfer, A.H. Knoll, S.M. McLennan, H.Y. McSween Jr., R.V. Morris, J.W. Rice Jr., R. Reider, and L.A. Soderblom. In situ evidence for an ancient aqueous environment at meridiani planum, mars. *Science*, 306:1709–1714, 2004.
- [13] R. Reider, R. Gellert, R.C. Anderson, J. Brückner, B.C. Clark, G. Dreibus, T. Economou, G. Klingelhöfer, G.W. Lugmair, D.W. Ming, S.W. Squyres, C. d'Uston, H. Wänke, A. Yen, and J. Zipfel. Chemistry of rocks and soils at meridiani planum from the alpha particle x-ray spectrometer. *Science*, 306:1746–1749, 2004.
- [14] M.S. Mohan and G.A. Rechnitz. Preparation and properties of the sulfate ion selective membrane electrode. *Analytical Chemistry*, 45:1323–1326, 1973.
- [15] G.A. Rechnitz, G.H. Fricke, and M.S. Mohan. Sulfate ion-selective membrane electrode. *Analytical Chemistry*, 44:1098–1099, 1972.
- [16] S. Lukow. *Design and characterization of ion selective electrode arrays for terrestrial and Martian soil analysis*. PhD thesis, Tufts University, 2005.
- [17] J.M. Boyce. *The Smithsonian Book of Mars*. Smithsonian Institute Press, 2002.
- [18] R.C. Quinn, J.D. Chittenden, S.P. Kounaves, and M.H. Hecht. The oxidation-reduction potential of aqueous soil solutions at the mars phoenix landing site. *Geophysical Research Letters*, 38:L14202, 2011.
- [19] M.H. Hecht, S.P. Kounaves, R.C. Quinn, S.J. West, S.M.M. Young, D.W. Ming, D.C. Catling, B.C. Clark, W.V. Boynton, J. Hoffman, L.P. DeFlores, K. Gospodinova, J. Kapit, and P.H. Smith. Detection of perchlorate and the soluble chemistry of martian soil at the phoenix lander site. *Science*, 325:64–67, 2009.
- [20] M.H. Lee, C.L. Yoo, J.S. Lee, I.-S. CHo, B.H. Kim, G.S. Cha, and H. Nam. Tweezer-type neutral carrier-based calcium-selective membrane electrode with drastically reduced anionic interference. *Analytical Chemistry*, 74:2603–2607, 2002.

- [21] R.L. Mancinelli. The search for nitrogen compounds on the surface of mars. *Advances in Space Research*, 18:241–248, 1996.
- [22] J.K. Johannesson and G.W. Gibson. Nitrate and iodate in antarctic salt deposits. *Nature*, 194:567, 1962.
- [23] W.L. Whitehead. The chilean nitrate deposits. *Economic Geology*, 15:187–224, 1920.
- [24] Böhlke, G.E. Ericksen, and K. Revesz. Stable isotope evidence for an atmospheric origin of desert nitrate deposits in northern chile and southern california, u.s.a. *Chemical Geology*, 136:135–152, 1997.
- [25] G. Michalski, J.K. Bohlke, and M. Thiemens. Long term atmospheric deposition as the source of nitrate and other salts in the atacama desert, chile: new evidence from mass-independent oxygen isotopic compositions. *Geochimica et Chosmochimica Acta*, 68:4023–4038, 2004.
- [26] M.M. Grady, I.P. Wright, and C.T. Pillinger. A search for nitrates in martian meteorites. *Journal of Geophysical Research*, 100:5449–5455, 1995.
- [27] W. V. Boynton, D. W. Ming, S. P. Kounaves, S. M. M. Young, R. E. Arvidson, M. H. Hecht, J. Hoffman, P. B. Niles, D. K. Hamara, R. C. Quinn, P. H. Smith, B. Sutter, D. C. Catling, and R. V. Morris. Evidence for calcium carbonate at the mars phoenix landing site. *Science*, 325:61–64, 2009.
- [28] R.C. Quinn. *Experimental characterization and in situ measurements of chemical processes in the martain surface environment*. PhD thesis, University of Leiden, The Netherlands, 2005.
- [29] V.F. Chevrier, J. Hanley, and T.S. Altheide. Stability of perchlorate hydrates and their liquid solutions at the phoenix landing site, mars. *Geophysical Research Letters*, 36:GL037497, 2009.
- [30] S.J. Wentworth, E.K. Gibson, M.A. Velbel, and D.S. McKay. Antarctic dry valleys and indigenous weathering in mars meteorites: Implications for water and life on mars. *Icarus*, 174:383–395, 2005.
- [31] D.M. Anderson, L.W. Gatto, and F.C. Ugolini. An antarctic analog of martian permafrost terrain. *Antarctic Journal of the United States*, 7:114–116, 1972.
- [32] K.A. Gibson, S.J. Wentworth, and D.S. McKay. Chemical weathering and diagenesis of cold desert soil from wright valley, antarctica: an analog of martian weathering processes. *Journal of Geophysical Research*, 88 supplement:A912–A928, 1983. Proceedings of the 13th lunar and planetary science conference, part 2 Feburary 15, 1983.

- [33] W.C. Mahaney, J.M. Dohm, R.V. Baker, H.E. Newsom, D. Malloch, R.G.V. Hancock, I. Campbell, D. Sheppard, and M.W. Milner. Morphogenesis of antarctic paleosols: Martian analogue. *Icarus*, 154:113–130, 2001.
- [34] D.R. Marchant and J.W. Head. Antarctic dry valleys: microclimate zonation, variable geomorphic processes, and implications for assessing climate change on mars. *Icarus*, 192:187–222, 2007.
- [35] I.B. Campbell and G.G.C. Claridge. *Antarctica: Soils, Weathering Processes and Environment*. Elsevier, 1987.
- [36] G.G.C. Claridge and I.B. Campbell. Origin of nitrate deposits. *Nature*, 217:428–430, 1968.
- [37] G.G.C. Claridge and I.B. Campbell. The salts in antarctic soils, their distribution and relationship to soil processes. *Soil Science*, 123:377–384, 1977.
- [38] J.G. Bockheim. Landform and soil development in the mcmurdo dry valleys, antarctica: a regional synthesis. *Arctic, Antarctic and Alpine Research*, 34:308–317, 2002.
- [39] C.P. McKay. Snow recurrence sets the depth of dry permafrost at high elevations in the mcmurdo dry valleys of antarctica. *Antarctic Science*, 21:89–94, 2009.
- [40] J.G. Bockheim and C. Tarnocai. Nature, occurrence and origin of dry permafrost. *Permafrost - Seventh International Conference (Proceedings)*, 1998.
- [41] W.W. Dickinson and K. Hopkins. *Preliminary report on soil and permafrost sampling: beacon, arena, and pearse valleys, dry valleys, antarctica, nov-dec 2001*. Antarctic Research Centre, 2005.
- [42] http://www.nasa.gov/images/content/226876main_5311.jpg.
- [43] http://www.nasa.gov/images/content/226875main_5305.jpg.
- [44] A.G. Fairén, A.F. Davila, D. Lim, N. Bramall, R. Bonaccorsi, J. Zavaleta, E.R. Uceda, C. Stoker, J. Wierzechos, J.M. Dohm, R. Amils, D. Andersen, and C.P. McKay. Astrobiology through the ages of mars: the study of terrestrial analogues to understand the habitability of mars. *Astrobiology*, 10:821–838, 2010.
- [45] J.J. Marlow, Z. Martins, and M.A. Sephton. Organic host analogues and the search for life on mars. *International Journal of Astrobiology*, 10:31–44, 2011.

- [46] R.A. Griffin and J.J. Jurinak. Estimation of acidity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. *Soil Science*, 116:26–30, 1973.
- [47] M Simón and I García. Physico-chemical properties of the soil-saturation extracts: estimation from electrical conductivity. *Geoderma*, 90:99–109, 1999.
- [48] J. R. Keys and Karen Williams. Origin of crystalline, cold desert salts in the mcmurdo region, antarctica. *Geochimica et Chosmochimica Acta*, 45:2299–2309, 1981.
- [49] J.G. Bockheim. Properties and classification of cold desert soils from antarctica. *Soil Science of America Journal*, 61:224–231, 1997.
- [50] W.J. Green, B.R. Stange, S. Wagers, J. Shacat, and S. Newell. Geochemical processes in the onyx river, wright valley, antarctica: Major ions, nutrients, trace metals. *Geochimica et Cosmochimica Acta*, 69:839–850, 2005.
- [51] **S. Stroble**, R. Anderson, Q. Moore, A. Morgenthaler, and S. Kounaves. (*in Preparation*), 2012.
- [52] S.P. Kounaves, **S.T. Stroble**, K. McElhoney, and G.D. ONeil. Comparison of the wet chemistry laboratory analysis of the phoenix mars lander with the antarctic dry valley soils, mars meteorite eeta79001 sawdust, and a mars stimulant. In *Mars Polar Science Conference, Fairbanks, Alaska*, 2011.
- [53] U.S. EPA, Federal Facilities Restoration and Reuse Office. *Emerging Contaminant - Perchlorate*, epa 505-f-09-005 edition, 2009. 4 pp.
- [54] A.B. Kirk. Environmental perchlorate: why it matters. *Analytica Chimica Acta*, 567:4–12, 2006.
- [55] G.E. Ericksen. Geology and origin of the chilean nitrate deposits. *U.S. Geolical Survey Professional Paper 1188*, page 37, 1981.
- [56] G.E. Ericksen, J.W. Hosterman, and P. St. Amand. Chemistry, mineralogy and origin of the clay-hill nitrate deposits, amargosa river valley, death valley region, california, u.s.a. *Chemical Geology*, 67:85–102, 1988.
- [57] G.J. Orris, G.J. Harvey, D.T. Tsui, and J.E. Eldrige. Preliminary analyses for perchlorate in selected natural materials and their derivative products. *United States Geological Survey, United States Department of the Interior. Open Field Report 03-314. pg. 6*, 2003.

- [58] P. B. Duncan, R. D. Morrison, and E. Vavricka. Forensic identification of anthropogenic and naturally occurring sources of perchlorate. *Environmental Forensics*, 6:205–215, 2005.
- [59] D. R. Parker, A. L. Seyfferth, and B. K. Reese. Perchlorate in groundwater: A synoptic survey of “pristine” sites in the coterminous united states. *Environmental Science and Technology*, 42:1465–1471, 2008.
- [60] W. A. Jackson, S.K. Anandam, T. Anderson, T. Lehman, K. Rainwater, K. Rainwater, S. Rajagopalan, M. Ridley, and R. Tock. Perchlorate occurrence in the texas southern high plains aquifer system. *Ground Water Monitoring & Remediation*, 25:137–149, 2005.
- [61] L.N. Plummer, J.K. Bohlke, and M.W. Doughten. Perchlorate in pleistocene and holocene groundwater in north-central new mexico. *Environmental Science and Technology*, 40:1757–1763, 2006.
- [62] S. Rajagopalan, T.A. Anderson, L. Fahlquist, K.A. Rainwater, M. Ridley, and W.A. Jackson. Widespread presence of naturally occurring perchlorate in high plains of texas and new mexico. *Environmental Science and Technology*, 40:3156–3162, 2006.
- [63] B. Rao, T.A. Anderson, G.J. Orris, K.A. Rainwater, S. Rajagopalan, R.M. Sandvig, B.R. Scanlon, D.A. Stonestrom, M.A. Walvoord, and W. A. Jackson. Widespread natural perchlorate in unsaturated zones of the southwestern united states. *Environmental Science and Technology*, 41:4522–4528, 2007.
- [64] V.I. Furdui and F. Tomassini. Trend and sources of perchlorate in arctic snow. *Environmental Science and Technology*, 44:588–592, 2010.
- [65] R. Simonaitis and J. Heicklen. Perchloric acid: a possible sink for stratospheric chlorine. *Planetary and Space Science*, 23:1567–1569, 1975.
- [66] S.S. Prasad and T.J. Lee. Atmospheric chemistry of the reaction $\text{ClO} + \text{O}_2$ to $\text{ClO} \bullet \text{O}_2$: where it stands, what needs to be done, and why? *Journal of Geophysical Research*, 99:8225–8230, 1994.
- [67] L. Jaeglé, Y.L. Yung, G.C. Toon, B. sen, and J.-F. Blavier. Balloon observations of organic and inorganic chlorine in the stratosphere: the role of HClO_4 production on sulfate aerosols. *Geophysical Research Letters*, 23:1749–1752, 1996.
- [68] P.K. Dasgupta, P.K. Martinelango, W.A. Jackson, T.A. Anderson, K. Tian, R.W. Tock, and S. Rajagopalan. The origin of naturally occurring perchlorate: the role of atmospheric processes. *Environmental Science and Technology*, 39:1569–1575, 2005.

- [69] N. Kang, T.A. Anderson, and W.A. Jackson. Photochemical formation of perchlorate from aqueous oxychlorine anions. *Analytica Chimica Acta*, 567:48–56, 2006.
- [70] N. Kang, W.A. Jackson, P.K. Dasgupta, and T.A. Anderson. Perchlorate production by ozone oxidation of chloride in aqueous and dry systems. *Science of the Total Environment*, 405:301–309, 2008.
- [71] N.C. Sturchio, M. Caffee, A.D. Beloso Jr., L.J. Heraty, J.K. Böhlke, P.B. Hatzinger, W.A. Jackson, B. Gu, J.M. Heikoop, and M. Dale. Chlorine-36 as a tracer of perchlorate origins. *Environmental Science and Technology*, 43:6934–6938, 2009.
- [72] W.A. Jackson, J.K. Böhlke, B. Gu, P.B. Hatzinger, and N.C. Sturchio. Isotopic composition and origin of indigenous natural perchlorate and co-occurring nitrate in the southwestern united states. *Environmental Science and Technology*, 44:4869–4876, 2010.
- [73] H. Bao, K.A. Jenkins, M. Khachatryan, and G.C. Diaz. Different sulfate sources and their post-depositional migration in atacama soil. *Earth and Planetary Science Letters*, 224:557–587, 2004.
- [74] D.C. Catling, M.W. Claire, K.J. Zahnle, R.C. Quinn, B.C. Clark, M.H. Hecht, and S. Kounaves. Atmospheric origins of perchlorate on mars and in the atacama. *Journal of Geophysical Research*, 115:E00E11, 2010.
- [75] D.P. Hautman, D.J. Munch, A.D. Eaton, and A.W. Haghani. Method 314.0: Determination of perchlorate in drinking water using ion chromatography. *U.S. Environmental Protection Agency*, pages 1–49, 1999.
- [76] S.P. Kouanves, **S.T. Stroble**, R.M. Anderson, Q. Moore, D.C. Catling, S. Douglas, C.P. McKay, D.W. Ming, P.H. Smith, L.K. Tamppari, and A.P. Zent. Discovery of perchlorate in the antarctic dry valleys and its global implications. *Environmental Science and Technology*, 44:2360–2364, 2010.
- [77] S.A. Ewing, B. Sutter, J. Owen, K. Nishiizumi, W. Sharp, S.S. Cliff, K. Perry, W. Diertich, C.P. McKay, and R.A. Amundson. A threshold in soil formation at earth’s arid-hyperarid transition. *Geochimica et Cosmochimica Acta*, 70:5293–5322, 2006.
- [78] C.C.-W. Lee, J. Sacarino, and M.H. Thiemes. Mass independent isotopic composition of atmospheric sulfate: origin and implications for the present and past atmosphere on earth and mars. *Geophysical Research Letters*, 28:1783–1786, 2001.
- [79] E.D. Lester, M. Satomi, and A. Ponce. Microflora of extreme arid atacama desert soils. *Soil Biology & Biochemistry*, 39:704–708, 2007.

- [80] S. A. Connon, E.D. Lester, H.S. Shafaat, D.C. Obenhuber, and A. Ponce. Bacterial diversity in hyperarid atacama desert soils. *Journal of Geophysical Research*, 112:G04S17, 2007.
- [81] B. Sutter, J.B. Dalton, S.A. Ewing, R. Andmunson, and C.P. McKay. Atacama spectral analogs for mars soils. *Journal of Geophysical Research*, 112:G04S10, 2007.
- [82] P. Mahaffy. Sample analysis at mars: developing analytical tools to search for a habitable environment on the red planet. *Geochemical News*, 141, 2009.
- [83] A.M. Skelley, J.R. Scherer, A.D. Aubrey, W.H. Grover, R.H.C. Ivester, P. Ehrenfreund, F.J. Grunthner, J.L. Bada, and R.A. Mathies. Development and evaluation of a microdevice for amino acid biomarker detection and analysis on mars. *Proceedings of the National Academy of Science*, 102:1041–1046, 2005.
- [84] R. Navarro-González, E. Vargas, J. de la Rosa, A.C. Raga, and C.P. McKay. Reanalysis of the viking results suggest perchlorate and organics at midlatitudes on mars. *Journal of Geophysical Research*, 115:E12010, 2010.
- [85] R.C. Quinn, A.P. Zent, F.J. Grunthner, P. Ehrenfreund, C.L. Taylor, and J.R.C. Garry. Detection and characterization of oxidizing acids in the atacama desert using the mars oxidation instrument. *Planetary and Space Science*, 53:1376–1388, 2005.
- [86] C.P. McKay. Two dry for life: the atacama desert and mars. *Ad Astra*, May-June:30–33, 2002.
- [87] C.P. McKay, E.I. Friedmann, B. Gómez-Silva, L. Cácered-Vilanueva, D.T. Andersen, and R. Landheim. Temperature and moisture conditions for life in the extreme arid region of the atacama desert: four years of observations including the el niño of 1997-1998. *Astrobiology*, 3:393–406, 2003.
- [88] H. Alonso and F. Risacher. Geochemistry of the salar de atacama, part 1: origin of the components and salt balance. *Revista Geologica de Chile*, 23:113–122, 1996.
- [89] V. Carmona, J.J. Pueyo, C. Taberner, G. Chong, and M. Thirlwall. Soluble inputs in the salar de atacama (n. chile). *Journal of Geochemical Exploration*, 69-70:449–452, 2000.
- [90] T. Boschetti, G. Cortecchi, M. Barbieri, and M. Mussi. New and past geochemical data on fresh to brine waters of the salar de atacama and andean altiplano, northern chile. *Geofluids*, 7:33–50, 2007.

- [91] F. Risacher, H. Alonso, and C. Salazar. The origin of brines and salts in Chilean salars: a hydrochemical review. *Earth-Science Reviews*, 63:249–293, 2003.
- [92] F. Risacher and B. Firtz. Origin of salts and brine evolution of Bolivian and Chilean salars. *Aquatic Geochemistry*, 15:123–157, 2009.
- [93] B. Gu and J.D. Coates, editors. *Perchlorate: Environmental Occurrence, Interactions and Treatment*. Springer, 2006.
- [94] M. Vega, G. Chong, and J.J. Pueyo. Parental brine evolution in the Chilean nitrate deposits (Pedro de Valdivia, 2^a región de Antofagasta). Mineralogical and petrographic data. In *Third ISAG*, 1996.
- [95] Walter H. Bortle. *Kirk-Othmer Encyclopedia of Chemical Technology*. Wiley-Interscience, 2000.
- [96] A.H. Rogers and H.R. Van Wagenen. The Chilean nitrate industry. In *Transactions of the American Institute of Mining Engineers*, 1918.
- [97] I.A. Berger and R.U. Cooke. Salts on alluvial fans in the Atacama Desert, northern Chile. *Earth Surface Processes and Landforms*, 22:581–600, 1997.
- [98] B.J. Buck, J. Rech, M. Howell, J. Prellwitz, and A.L. Brock. A new formation process for patterned ground, Atacama Desert, Chile. In *2006 Philadelphia Annual Meeting. The Geological Society of America. Paper No. 216-8*, 2006.
- [99] D.R. Lide, editor. *Handbook of Chemistry and Physics*. CRC Press, 82nd edition, 2001.
- [100] D.R. Bagaley. Uncovering bacterial diversity on and below the surface of a hyper-arid environment, the Atacama Desert, Chile. Master's thesis, Louisiana State University, 2006.
- [101] H. Bao and D.R. Merchant. Quantifying sulfate components and their variations in soils of the McMurdo Dry Valleys, Antarctica. *Journal of Geophysical Research*, 2:D16301, 2006.
- [102] H. Bao and M.C. Reheis. Multiple oxygen and sulfur isotopic analysis on water-soluble sulfate in bulk atmospheric deposition from the southwestern United States. *Journal of Geophysical Research*, 108:D144430, 2003.
- [103] K. Al-Barrak and D.L. Rowell. The solubility of gypsum in calcareous soils. *Geoderma*, 136:830–837, 2006.

- [104] K.A. Welch, W.B. Lyons, E. Graham, K. Neumann, J.M. Thomas, and D. Mikesell. Determination of major element chemistry in terrestrial waters from antarctica by ion chromatography. *Journal of Chromatography A*, 739:257–263, 1996.
- [105] U.S. Salinity Laboratory Staff. Diagnosis and improvement of saline and alkali soils. *U.S. Department of Agriculture, Handbook Number 60:160 pp.*, 1954.
- [106] P. H. Smith, L. K. Tamppari, R. E. Arvidson, D. Bass, D. Blaney and W. V. Boynton, A. Carswell, D. C. Catling, B. C. Clark, T. Duck, E. DeJong, D. Fisher, W. Goetz, H. P. Gunnlaugsson, M. H. Hecht, V. Hipkin, J. Hoffman, S. F. Hviid, H. U. Keller, S. P. Kounaves, C. F. Lange, M. T. Lemmon, M. B. Madsen, W. J. Markiewicz, J. Marshall, C. P. McKay, M. T. Mellon, D. W. Ming, R. V. Morris, W. T. Pike, N. Renno, U. Staufer, C. Stoker, P. Taylor, J. A. Whiteway, and A. P. Zent. H₂O at the phoenix landing site. *Science*, 325:58–61, 2009.
- [107] *Mars: The NASA Mission Reports Volume 1*. Apogee Books, 2000.
- [108] *Mars The NASA Mission Reports Volume 2*. Apogee Books, 2004.
- [109] R. Navarro-González, K.A. Navarro, J. de la Rosa, E. Iniguez, P. Molina, L.D. Miranda, P. Morales, E. Cienfuegos, P. Coll, F. Raulin, R. Amils, and C.P. McKay. The limitations on organic detection in mars-like soils by thermal volatilization-gas chromatography-ms and their implications for the viking results. *Proceedings of the National Academy of Science*, 103:16089–16094, 2006.
- [110] G.J. Flynn. The delivery of organic matter from asteroids and comets to the early surface of mars. *Earth, Moon, and Planets*, 72:469–474, 1996.
- [111] R. Navarro-González, E. Iniguez, J. de la Rosa, and C.P. McKay. Characterization of organics, microorganisms, desert soils, and mars-like soils by thermal volatilization coupled to mass spectrometry and their implications for the search for organics on mars by phoenix and future space missions. *Astrobiology*, 9:703–715, 2009.
- [112] I.A. Shkrob, S.D. Chemerlsov, and T.W. Marin. Photocatalytic decomposition of carboxylated molecules on light-exposed martian regolith and its relation to methane production on mars. *Astrobiology*, 10:425–436, 2010.
- [113] S.A. Benner, K.G. Devine, L.N. Matveeva, and D.H. Powell. The missing organic molecules on mars. *Proceedings of the National Academy of Science*, 97:2425–2430, 2000.

- [114] N.H. Horowitz, A.J. Bauman, R.E. Cameron, P.J. Geiger, J.S. Hubbard, G.P. Shulman, P.G. Simmonds, and K. Westburg. Sterile soil from antarctica: organic analysis. *Science*, 164:1054–1056, 1969.
- [115] R. Navarro-González, F.A. Rainey, P. Molina, D.R. Bagaley, B.J. Hollen, J. de la Rosa, A.M. Small, R.C. Quinn, F.J. Gunthamer, L. Cáceres, B. Gomez-Silva, and C.P. McKay. Mars-like soils in the atacama desert, chile, and the dry limit of microbial life. *Science*, 302:1018–1021, 2003.
- [116] W. V. Boynton, S.H. Bailey, D.K. Hamara, M.S. Williams, R.C. Bode, M.R. Fitzgibbon, W.J. Ko, M.G. Ward, K.R. Sridhar, J.A. Blanchard, R.D. Lorenz, R.D. May, D.S. Paige, A.V. Pathare, D.A. Kring, L.A. Leshin, D.W. Ming, A.P. Zent, D.C. Golden, K.E. Kerry, H. Vern Lauer, and R.C. Quinn. Thermal and evolved gas analyzer: Part of the mars volatile and climate surveyor integrated payload. *Journal of Geophysical Research - Planets*, 106:683–17, 2001.
- [117] J.H. Hoffman, R.C. Chaney, and H. Hammack. Phoenix mars mission: The thermal evolved gas analyzer. *Journal of the American Society of Mass Spectrometry*, 19:1377–1383, 2008.
- [118] B.E. DiGregorio. The search for organic molecules. *Analytical Chemistry*, 77:348A–353A, 2005.
- [119] S.K. Atreya, P.R. Mahaffy, and A.-S. Wong. Methane and related species on mars: origin, loss, implications for life, and habitability. *Planetary and Space Science*, 55:358–369, 2007.
- [120] P. Mahaffy. Exploration of the habitability of mars: Development of analytical protocols for measurement of organic carbon on the 2009 mars science laboratory. *Space Science Reviews*, 135:255–268, 2008.
- [121] P. Coll, F. Goesmann, F. Raulin, L. Becker, C. Szopa, A. Buch, V. Pinnick, S. Harald, R. Sternberg, C. Freissinet, O. Roders, N. Grand, E. Reynolds, D. Coscia, J.J. Correia, P. Granier, B. Lustrent, M. Jerome, C. Philippon, E. Steinmetz, I. Krause, M. Bierwirth, S. Jaskulek, E. Adams, M. Antoine, T. Cornish, G. Ellers, P. Hogue, and K. Strobehn. How moma will search for life bio-indicators at mars in 2018. In *38th COSPAR Scientific Assembly*, 2010.
- [122] L. Becker. Moma: mars organic molecule analyzer. In *The 7th Workshop on Harsh-Environment Mass Spectrometry, Santa Barbara, CA*, 2009.
- [123] T. Evens-Nguyen, L. Becker, V. Doroshenko, and R.J. Cotter. Development of a low power, high mass range mass spectrometer for mars surface analysis. *International Journal of Mass Spectrometry*, 278:170–177, 2008.

- [124] Max Planck Institute for Solar System Research. <http://www.mps.mpg.de/de/projekte/exomars/moma/index.html>.
- [125] W. Goetz, H. Steininger, E. Steinmetz, M. Bierwith, F. Goesmann, C. Phillippon, B. Lustrement, C. Szopa, A. Bush, H. Admunsen, M. Fogel, and A. Steele. Mars organic molecule analyzer (moma) field tests as part of amase 2010 svalbard expedition. In *2nd Lunar and Planetary Science Conference in The Woodlands, TX.*, 2011.
- [126] J.L. Bada, P. Ehrenfreund, F. Grunthner, D. Blaney, M. Coleman, A. Farrington, A. Yen, R. Mathies, R. Amudson, R. Quinn, A. Zent, S. Ride, L. Barron, O. Botta, B. Clark, D. Glavin and B. Hofmann, J.L. Josset, R. Rettberg, F. Robert, and M. Sephton. Urey: Mars organic and oxidant detector. *Space Science Review*, 135:269–279, 2008.
- [127] A.M. Skelley, A.D. Aubrey, P.A. Willis, X. Amashukeli, P. Ehrenfreund, J.L. Bada, F.J. Grunthner, and R.A. Mathies. Organic amine biomarker detection in the yungay region of the atacama desert with the urey instrument. *Journal of Geophysical Research*, 112:G04S11, 2007.
- [128] E.T. Urbanski. Total organic carbon analyzers as tools for measuring carbonaceous matter in natural waters. *Journal of Environmental Monitoring*, 3:102–112, 2001.
- [129] I. Bisutti, I. Hilke, and M. Raessler. Determination of total organic carbon - an overview of current methods. *Trends in Analytical Chemistry*, 23:716–726, 2004.
- [130] D.W. Hendricks. *Water Treatment Unit Processes: Physical and Chemical*. CRC Press, 2006.
- [131] K.A. Clark. Total organic carbon analysis for cleaning validation in pharmaceutical manufacturing. *International Society for Pharmaceutical Engineering*, October 2000.
- [132] I. Lerche. *Geological Risk and Uncertainty in Oil Exploration*. Academic Press, 1997.
- [133] N. Khan-Mayberry, J.T. James, R. Tyl, and C. w. Lam. Space toxicology: protecting human health during space operations. *International Journal of Toxicology*, 30:3–18, 2011.
- [134] A.L. Clements, R.G. Stinson, M. van Wie, and E. Warren. Development of the second generation international space station (iss) total organic carbon analyzer (toca). *SAE International Journal of Aerospace*, 4:219–226, 2011.

- [135] S.A. Ewing, J.L. Macalady, K. Warren-Rhodes, C.P. McKay, and R. Amundson. Changes in the soil c cycle at the arid-hyperarid transition in the atacama desert. *Journal of Geophysical Research*, 113:G02S90, 2008.
- [136] G.M. Marion, P.S.J. Verberg, E.V. McDonald, and J.A. Arnone. Modeling salt movement through a mojave desert soil. *Journal of Arid Environments*, 72:1012–1033, 2008.
- [137] C.V. Haynes Jr. Geochronology and climate change of the pleistocene-holocene transection in the darb el arba'in desert, eastern sahara. *Geochronology*, 16:119–141, 2001.
- [138] X. Amashukeli, F.J. Grunthaler, S.B. Partrick, and P.T. Yung. Subcritical water extractor for mars analog soil analysis. *Astrobiology*, 8:597–604, 2008.
- [139] M.B. Burkins, R.A. Virginia, C.P. Chamberlain, and D.H. Wall. Origin and distribution of soil organic matter in taylor valley, antarctica. *Ecology*, 8:2377–2391, 2000.
- [140] D.L. Moorhead, J.E. Barrett, R.A. Virginia, D.H. Wall, and D. Porazinska. Organic matter and soil biota of upland wetlands in taylor valley, antarctica. *Polar Biol.*, 26:567–576, 2003.
- [141] J.E. Barrett, R.A. Virginia, A.N. Parsons, and D.H. Wall. Potential soil organic matter turnover in taylor valley, antarctica. *Arctic, Antarctic, and Alpine Research*, 37:108–117, 2005.
- [142] J.E. Barrett, M.N. Gooseff, and C. Takacs-Vesbach. Spatial variation in soil active-layer geochemistry across hydrologic margins in polar desert ecosystems. *Hydrology and Earth Systems Science*, 13:2349–2358, 2009.
- [143] D.W. Hopkins, A.D. Sparrow, E.G. Gregorich, B. Elberling, P. Novis, F. Fraser, C. Scrimgeour, P.G. Dennis, W. Meier-Augenstein, and L.G. Greenfield. Isotopic evidence for the provenance and turnover of organic carbon by soil microorganisms in the antarctic dry valleys. *Environmental Microbiology*, 11:597–608, 2009.
- [144] W.B. Lyons, K.A. Welch, and J.K. Doggett. Organic carbon in antarctic snow. *Geophysical Research Letters*, 34:L02501, 2007.
- [145] G.I. Matsumoto, E. Honda, K. Sonoda, S. Yamamoto, and T. Takemura. Geochemical features and sources of hydrocarbons and fatty acids in soils from the mcmurdo dry valleys in the antarctica. *Polar Science*, 4:187–196, 2010.

- [146] B. Eberling, E.G. Gregorich, D.W. Hopkins, A.D. Sparrow, P. Novis, and L.G. Greenfield. Distribution and dynamics of soil organic matter in the antractic dry valley. *Soil Biology & Biochemistry*, 38:3095–3106, 2006.
- [147] A. Fujishima, Y. Einaga, T.N. Eao, and D.A. Tryk, editors. *Diamond Electrochemistry*. Elsevier, 2005.
- [148] W. Fabinski, G. Wiegleb, P. Hering, W. Fuss, and M. Haisch. *Non-dispersive infrared spectrometer*. Patent Number: 5,486,699, 1996.
- [149] D.J. Eckstrom. *NDIR apparatus and method for measuring isotopic ratios in gaseous samples*. Patent Number: 5,747,809, 1998.
- [150] <http://www.omega.com/manuals/manualpdf/m0783.pdf>.
- [151] A. P. Zent, R. C. Quinn, J. L. Lambert, S. Kounaves, S. Young, J. Bell, M. Hecht, and C. Taylor. Measurement of total organic and total inorganic carbon on mars. In *37th Lunar and Planetary Science Conference: Abstract 2184*, 2006.
- [152] **S. Stroble** and S. Kounaves. (*in Preparation*), 2012.
- [153] http://www.nasa.gov/topics/aeronautics/features/trl_demystified.html.
- [154] C. Comninellis and G. Chen, editors. *Electrochemistry for the Environment*. Springer, 2010.
- [155] M. Panizza and G. Cerisola. Application of diamond electrodes to electrochemical processes. *Electrochimica Acta*, 51:191–199, 2005.
- [156] A.E. Fischer, Y. Show, and G.M. Swain. Electrochemical performance of diamond thin-film electrodes from different commercial sources. *Analytical Chemistry*, 76:2553–2560, 2004.
- [157] P.W. May. Cvd diamond: a new technology for the future? *Endeavor*, 19:101–106, 1995.
- [158] M. Hupert, A. Muck, J. Wang, J. Stotter, Z. Cvackova, S. Haymond, Y. Show, and G. M. Swain. Conductive diamond thin-films in electrochemistry. *Diamond and Related Materials*, 12:1940–1949, 2003.
- [159] J. Park, V. Quaiserova-Mocko, B. A. Patel, M. Novotny, A. Liu, X. Bian, J.J. Galligan, and G. M. Swain. Diamond microelectrodes for in vitro electroanalytical measurements: current status and remaining challenges. *Analyst*, 133:17–24, 2008.
- [160] Y. Tian, X. Chen, C. Shang, and G. Chen. Active and stable ti/si/bdd anodes for electro-oxidation. *Journal of the Electrochemical Society*, 153:J80–J85, 2006.

- [161] J. Herlinger. *sp³'s experience using hot filament cvd reactors to grow diamond for an expanding set of applications*. sp³ Diamond Technologies, 2004.
- [162] J. Mort, D. Kuhman, M. Machonkin, M. Morgan, F. Jansen, K. Okumura, Y.M. LeGrice, and R.J. Nemanich. Boron doping of diamond thin films. *Applied Physics Letters*, 55:1121–1125, 1989.
- [163] J. Mort, M.A. Machonkin, and K. Okumura. Infrared absorption in boron-doped diamond thin films. *Applied Physics Letters*, 58:1908–1910, 1991.
- [164] M. Werner and R. Locher. Growth and application of undoped and doped diamond. *Reports on Progress in Physics*, 61:1665–1710, 1998.
- [165] S. Koizumi, C.E. Nebel, and M. Nesladek, editors. *Physics and applications of CVD diamond*. Wiley-VCH, 2009.
- [166] J.S. Lewis. *Physics and Chemistry of the Solar System*, volume 87. Academic Press, 2 edition, 2004.
- [167] M.H. Engel and S.A. Macko. Isotopic evidence for extraterrestrial non-racemic amino acids in the murchison meteorite. *Nature*, 389:265–268, 1997.
- [168] K. Kvenvolden, J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnampereuma, I.R. Kaplan, and C. Moore. Evidence for extraterrestrial amino acids and hydrocarbons in the murchison meteorite. *Nature*, 228:923–926, 1970.
- [169] J.G. Lawless. Amino acids in the murchison meteorite. *Geochimica et Cosmochimica Acta*, 37:2207–2212, 1973.
- [170] J. Oró, J. Gibert, H. Lichtenstein, S. Wikstrom, and D.A. Flory. Amino acids, aliphatic and aromatic hydrocarbons in the murchison meteorite. *Nature*, 230:105–106, 1971.
- [171] S. Pizzarello, Y. Huang, and M. Fuller. The carbon isotopic distribution of murchison amino acids. *Geochimica et Cosmochimica Acta*, 68:4963–4969, 2004.
- [172] J.L Bada, D.P. Clavin, G.D. McDonald, and L. Becker. A search for endogenous amino acids in martian meteorite alh84001. *Science*, 279:362–365, 1998.
- [173] D. Gandini, E. Mahe, P.A. Michaud, W. Haenni, A. Perret, and Ch. Comninellis. Oxidation of carboxylic acids at boron-doped diamond electrodes for wastewater treatment. *Journal of Applied Electrochemistry*, 30:1345–1350, 2000.

- [174] P. Canizares, J. Garcia-Gomez, J. Lobato, and M. A. Rodrigo. Electrochemical oxidation of aqueous carboxylic acid wastes using diamond thin-film electrodes. *Industrial & Engineering Chemistry Research*, 42:956–962, 2003.
- [175] J.-F. Zhi, H.-B. Wang, T. Nakashima, T.N. Rao, and A. Fujishima. Electrochemical incineration of organic pollutants on boron-doped diamond electrode evidence for direct electrochemical oxidation pathway. *Journal of Physical Chemistry B*, 107:13389–13395, 2003.
- [176] S.W. Squyres, R.E. Arvidson, J.F. Bell, J. Bruckner, N.A. Cabrol, W. Calvin, M.H. Carr, P.R. Christensen, B.C. Clark, L. Crumpler, D.J. Des Marais, C. dUston, T. Economou, J. Farmer, W. Farrant, W. Folkner, M. Golombek, S. Gorevan, J.A. Grant, R. Greeley, J. Grotzinger, L. Haskin, K.E. Herkenhoff, S. Hviid, J. Johnson, G. Klingelhofer, A. Knoll, G. Landis, M. Lemmon, R. Li, M.B. Madsen, M.C. Malin, S.M. McLennan, H.Y. McSween, D.W. Ming, J. Moersch, R.V. Morris, T. Parker, J.W. Rice Jr., L. Richter, R. Rieder, M. Sims, M. Smith, P. Smith, L.A. Soderblom, R. Sullivan, H. Wanke, T. Wdowiak, M. Wolff, and A. Yen. The spirit rover's athena science investigation at gusev crater, mars. *Science*, 794:794–799, 2004.
- [177] M.A. Kessler and B.T. Werner. Self-organization of sorted patterned ground. *Science*, 299:380–383, 2003.
- [178] Frank Press and Raymond Siever. *Understanding Earth*. W.H. Freeman and Company, 3 edition, 2001.