Examination of 24 Martian rock and soil classes using GUAPX software and the K-value approach on MER-A APXS results for possible hydration or ALICs

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Examination of 24 Martian rock and soil classes using GUAPX software and the K-value approach on MER-A APXS results for possible hydration or ALICs

Paso Robles soil class is proven to be significantly hydrated (Campbell et al., 2008). Numerous other Martian soil and rock classes identified by MER-A APXS have not been previously examined for the presence of possible ALICs. The goal of this project was to detect the possible presence of ALICs in a group of selected classes using experimental C/R values obtained from GUAPX software and by employing the comprehensive K-value analytical technique. K-values for Gertrude Weise and Elizabeth Mahon classes were significantly lower that the calibration standard average K-value of 0.91. K-values for all other classes were within or higher than the K-value average zone (0.87-0.95). The GUAPX plots were insufficient in detecting the presence of possible ALICs. The K-value results indicated that rock class Elizabeth Mahon and soil class Gertrude Weise contained possible ALICs in orders of magnitude similar to Paso Robles which contains 6-18 wt% hydration (Campbell et al., 2008). All other rock and soil classes analysed failed to reveal possible ALICs in the K-value plots. The levels of ALICs in these classes may be below the detection limit or they may not contain mineralogically bound water despite the role of past aqueous alterations in their formation.

Abbreviations: MER-A (Mars Exploration Rovers, A: Spirit, B: Opportunity); APXS (Alpha Particle X-Ray Spectrometer); PIXE (Particle Induced X-Ray Emission); XRF (X-Ray Fluorescence); ALICs (Additional Light Invisible Components); C/R (Compton-Rayleigh ratio); F[I] (Fraction of Invisibles)

1. Introduction

NASA’s Mars Exploration Rovers, Spirit & Opportunity have sampled many Martian rock and soil targets since the launch of the mission in 2003. The goal of this robotic space mission was to examine the Martian geology and characterize the Martian rocks and soils to uncover clues for past or present water activity. The Opportunity rover is still active as of 2013 but its twin; Spirit became immobile and ceased communications in 2010 (JPL, NASA). However, over the six years of Spirit’s journey on Mars, it has examined over 300 rock and soil targets with the help of its scientific payload. These samples have then been classified into specific rock and soil classes based on their elemental composition as determined by their APXS spectra (Gellert et al., 2006). Various subsequent studies have stressed on the possible importance of aqueous activities in the formation of many of these rocks and soil classes (Ming et al., 2006). For example, according to Clark et al., 2007, the rock class Independence contains smectite or smectite-like phases that were possibly a result of past aqueous alterations. The spectral features of soil class Gertrude Weise indicated opaline-silica deposits that are believed to be produced due to aqueous processes as well (Ruff et al., 2011). Extensive further research was conducted for soil class
Paso Robles by Campbell et al., 2008. Their results indicated that Paso Robles were indeed highly hydrated soils with up to 6-18 wt% mineralogically bound water.

Similar extensive research is lacking for many other MER-A Martian rock and soil classes that are believed to have undergone aqueous alterations in the past. This research project aimed to similarly examine some of these rocks and soil classes that have not been previously analysed for possible hydration or ALICs. The two objectives for this project were: 1. to test whether the experimental C/R values extracted from the GUAPX software alone were capable of indicating possible ALICs in the selected classes and 2. to detect the presence of possible ALICs in selected classes using the more comprehensive K-value approach.

2. MER-A: Spirit Rover

Spirit, a six-wheeled solar-powered robot (Figure 1) is one of the two rovers built for the Mars exploration mission. The rover was launched on June 10, 2003 and landed on Mars at the Columbia Memorial Station near the Gusev Crater on January 4, 2004 (JPL, NASA) (Figure 2.A).

Figure 1. A computer-generated image of MER-A Spirit rover on Mars (JPL, NASA).

Figure 2.A) The entire journey of MER-A Spirit rover on Mars, from the landing site Columbia Memorial Station to Troy, near Home Plate. B) A close-up of the Home Plate region (JPL, NASA).
The rover proceeded to travel approximately three kilometres across to an area of low-lying
hills known as the Columbia Hills and then to the Home Plate region (Figure 2.B). Spirit was
initially planned for only a short 90-sol mission but performed significantly longer than planned;
it covered around 4.8 miles. This is attributed to the dust whirlwinds the rover encountered on
March 9, 2005. The intense whirlwinds cleaned the rovers’ solar panels and this dramatically
increased the power levels. However, the rover became stuck on May 6, 2009 near Troy when it
encountered a thick layer of loose sediment. The sediments were camouflaged beneath the
surface with the red Martian dust that covers most of the planet. The rover’s wheels where
unable to obtain a grip when they encountered this sediment with low cohesion. Several
extrication drives were performed but they were unable to free the rover. On January 26, 2010 it
was announced that the rover would continue to function as a stationary scientific platform.
Communications with Spirit were lost on March 22, 2010. This is attributed to extremely low
power supplies and very low internal temperatures due to the rover being stuck on an exposed
flat ground during winter. Repeated attempts were made by the Jet Propulsion Laboratory to
regain the communications but on January 26, 2010, the rover was pronounced immobile and
inactive (JPL, NASA).

Figure 3. Diagram of MER-A Spirit rover outlining the scientific payload it carries (JPL, NASA).

Spirit’s goal was to essentially ‘follow the water’ on Mars. The mission was to characterize
various rocks and soils in order to uncover clues for past aqueous activities on Mars, including
their distribution and elemental composition. This was achieved with the scientific payload
(Figure 3) onboard the rover which included a) two Hazcams that provided data about the rovers
surroundings, b) a Navigation Camera (Navcam) used for navigating and driving the rover, c) a
Panoramic Camera (Pancam) that examined the colour and texture of the terrain, d) a Miniature
Thermal Emission Spectrometer (mini-TES) that identified interesting rocks and soils for
examination, e) a Rock Abrasion Tool (RAT) that exposed geologic material to be examined by the instruments, f) a Microscopic Imager (MI) that obtained high-resolution images of the samples, g) a Mossbauer Spectrometer that closely examined the mineralogy of iron bearing rocks and soils and most importantly, h) the Alpha Particle X-ray Spectrometer (APXS), an instrument that revealed the elemental composition and abundances of the samples (*JPL, NASA*).

3. APXS Instrument

The APXS instrument was developed by the Max Planck Institute in Germany and is located on the instrument deployment arm of the Spirit rover. It allowed for the *in-situ* detection and quantification of the elemental composition of Martian rocks & soil samples using alpha particles and x-rays from a radioactive source. The six small radioactive sources onboard Spirit’s APXS is Curium-244 (*JPL, NASA*).

![Figure 4](image-url)  
**Figure 4.** MER Alpha Particle X-ray Spectrometer (APXS) sensor head (*JPL, NASA*).

The scientific target is made to come in contact with the APXS instrument (*Figure 4*) and the sample is irradiated with incident alpha particles and x-rays resulting from the decay of Cm-244. The scattered alpha particles and fluorescent X-rays are detected by the instrument and the resultant energy distribution or spectrum reveals the elemental composition of the sample. This elemental composition of Martian rocks and soils are crucial for determining the processes that resulted in their formation and the possibilities of past water activities.
The alpha particles from Cm-244 decay are capable of exciting lower atomic weight elements, from Na to Ca. The X-rays from the daughter Plutonium are capable of exciting heavier elements, from Ca to Zr. These two modes of excitation are PIXE and XRF respectively. Combined, these two techniques give the APXS a very well-balanced sensitivity with a detection range of Na to Zr (Bruckner et al., 2008) (Figure 5).

During Particle Induced X-Ray Emission (PIXE), the incident alpha particle hits an inner or lower energy shell (K- and L- shell) electron in the atoms of the target sample and causes the electron to be ejected. To re-stabilize the atom, an electron from a higher energy level migrates to take up this vacancy and in this process the atom releases a characteristic X-ray. Different elemental atoms within a sample have their own characteristic electron shell configurations and when the higher energy shell electron migrates to fill the vacancy, energy is released. This characteristic energy is the difference between the energies of the two electron orbits involved. Therefore, the resultant X-ray has a characteristic energy that is specific to the element. X-ray fluorescence (XRF) is similar in technique to PIXE but instead of an incident alpha particle, an incident X-ray hits the electrons. These techniques are the basis of the elemental peaks seen on an APXS spectrum.
When observing the peaks on a typical APXS spectrum (Figure 6), two distinct scatter peaks can also be observed. These are the inelastic (Compton) and elastic (Rayleigh) scatter peaks. During Compton scattering, a photon is in-elastically scattered off an electron. The photon transfers some of its own energy to the electron and causes the electron to be excited. The excited electron recoils and is ejected. Thus, the resultant degraded photon has a lower energy and a longer wavelength than the incident photon due to the loss of the electron. The shifts in wavelengths increase with the increase in the angle of scattering. Rayleigh scattering occurs when an incident ray is elastically deflected of an atom, without a change in its frequency or energy. Thus, there is no loss of electrons and the scattered ray has the same energy and wavelength as the incident ray.

These scatter peaks play a significant role in the detection of light elements, lighter than atomic number 11 (< Na), also known as Additional Light Invisible Components (ALICs) (Glynis Perrett). The ratio of Compton and Rayleigh scatter intensities can be extracted from the GUAPX software by appropriately fitting the APXS spectra using various model functions. These experimental C/R values, when compared to similar simulated values allows for the detection of the possible presence of ALICs. This comprehensive analysis is known as the K-value approach.

4. Methodology

The APXS spectra of MER-A Martian soil and rock classes selected for this project were fitted in the GUAPX software to extract their experimental C/R values. Simulated C/R values were also obtained from the MarsGeom software. The experimental and simulated C/R values were then compared to detect the presence of ALICs.
4.1 Selection of Rock and Soil Classes

Numerous research papers focussing on soil and rock classes examined by MER-A (Spirit) were collected and read. All rock and soil classes and their sub-classes mentioned in these papers were recorded (see Appendix). From this list, twenty rock classes and five soil classes were then selected. The selection criteria for these classes were, a) they had to be classes examined by the Spirit rover on Mars, b) they were not previously analysed and c) the literature proposed some form of past aqueous alterations in their formation. Based on this the rock classes selected were: Adirondack, Clovis, Wishstone, Peace, Watchtower, Methuselah, Jibsheet, Backstay, Independence, Decartes, Irvine, Seminole, Algonquin, Comanche, Barnhill, Posey, Halley, Montlava, Torquas and Elizabeth Mahon. The soil classes selected were: Gertrude Weise, Eileen Dean, Paso Robles, Laguna and Home Plate. The various samples targeted by the APXS within each class were also obtained from the literature and recorded, along with their sol (Martian date when the sample was examined by the APXS). The APXS spectra for all these samples from the selected classes were then obtained from JPL, NASA; Dr. R. Gellert and Dr. J. L. Campbell.

![Figure 7. A) Table showing 3 samples (Paso Robles, Paso Robles Light & Dead Sea Samra) from the Paso Robles soil class and their weight% hydration. B) Photograph of the bright Paso Robles material (Campbell et al., 2008).](image)

The soil class Paso Robles (Figure 7.B) was specifically selected to be used as a comparative standard against the rest of the selected rock and soil classes. This was done because Paso Robles is a highly hydrated ferric sulphate soil with 49 wt% ferric sulphate. Using the K-value approach, they are proven to contain 6-18 wt% bound water (Campbell et al., 2008) (Figure 7.A). They are high in sulphur, iron (16.3 wt%) and phosphorus (2.4 wt%). Their mineralogy and chemistry strongly suggest past aqueous alteration processes (Bruckner et al., 2008). According to Campbell et al., 2008, their formation is similar to an evaporate deposit formed from solutions rich in iron, sulphur, magnesium, calcium and phosphorus. Bruckner et al., 2008, suggests that they are likely hydrothermal deposits formed as a result of magma degassing on Mars.

Therefore, Paso Robles was an appropriate selection as a comparative class since a) they are proven to be hydrated soils, b) they have a high magnitude of hydration and c) they were examined using the K-value approach as well.
4.2 Fitting Spectra in GUAPX Software

The selected APXS spectra files were fitted in the GUAPX software. This computer software package had been developed by Dr. J. L. Campbell and his team at the University of Guelph. This is a revised version on the GUPIX software which could only fit the PIXE component of the spectrum. The new GUAPX software is capable of fitting the entire spectrum, including both the PIXE and XRF components. The spectra files had to be modified with the correct channel length (512 0) and file format (.sdf) to be compatible with the current version of software used, GUAPX-V1.8.MER. The model functions used included: a) full Pu scatter peaks, b) 32.7mm CO$_2$ length and 8.5mbar CO$_2$ pressure, c) H-value of 0.442 for H calibration (single instrument constant), d) samples were assumed to be infinitely thick, e) depth fraction of 0.9 for X-ray production depth and 2.75gm/cm$^3$ target density, f) O$_2$ as the dependant invisible element and g) 26 to 510 channel range for the region of fit.

![Data and Fit vs. Channel](image)

*Figure 8.* An APXS spectrum after fitting in GUAPX software.

The resultant output was examined to ensure a proper fit. Elements like Rubidium (Rb) and Strontium (Sr) were both or individually removed in some cases to improve the fit because the scatter peaks of Rb and Sr overlap the Compton and Rayleigh peaks. This was done to ensure that the Compton and Rayleigh values extracted were not influenced by the intensities of the Rb and Sr peaks. Once a satisfactory fit was obtained with low residual standard deviations (*Figure 8*), the run duration, the C/R values and the one sigma %error data were extracted and recorded. Seventy such fits were performed to include sufficient samples from each rock and soil class. This was the basis for the experimental C/R data for the project. A mega-file encompassing the elemental composition and concentration for each of the seventy fits were also created.

4.3 Performing Simulations in MarsGeom Software

Monte Carlo simulations are used to approximate the probability of certain outcomes and it is performed by running multiple trial runs or simulations with various variables. Monte Carlo simulations were performed for each of the seventy rocks and soil samples using the MarsGeom software. This thorough simulation package was developed by Dr. J. L. Campbell, Dr. C. L. Mallet and Dr. J. M. O’Meara to extract predicted C/R values.
In order to perform the simulations in this software, compatible files known as ‘PARfiles’ were created for each of the seventy samples using elemental concentration data from the GUAPX mega-files. The variables or criteria set for the simulations were, a) generation of 40 billion photons and b) set Oxygen at 0%. Each of the seventy simulations ran for approximately 12-16 hours. Every one of these 40 billion photons was tracked through single and multiple scatter events. The sum of all the single Rayleigh scatter events generated the Rayleigh value and the sum of the entire single and multiple Compton scatter events generated the Compton value. This simulation process generated ‘RMG’ output files with the expected C/R scatter ratio for the Pu L-alpha X-rays and the one sigma standard error value, which were extracted and recorded.

4.4 Data Analysis

For objective 1, the experimental C/R values extracted from the GUAPX software were plotted against the ‘Fraction of Invisibles’ (F[I]) with appropriate error bars. The F[I] values are essentially the Oxygen concentration weight% that were obtained from the mega-files created during the fitting of spectra in GUAPX. Also, the one sigma %error data for the experimental C/R ratios were converted to two sigma absolute errors before plotting. A linear trend line was generated using all the plotted rocks and soil classes.

For objective 2, first, the one sigma absolute errors associated with the simulated C/R values were converted to two sigma absolute errors. Then, K-values were calculated for each of the seventy samples by comparing the experimental C/R values to the simulated C/R values (the simulated C/R values were divided by the experimental C/R values). These K-values were plotted against the F[I] obtained previously for each rock and soil class along with appropriate error bars. These K-value errors were calculated by taking the power of experimental error divided by experimental C/R and adding that to the power of simulated error divided by the simulated C/R. Then, the square root of the resultant value was multiplied by the K-value for that sample to generate the K-value errors. A calibration standard K-value of 0.91 with +/- 0.04 errors (Dr. J. L. Campbell, Catherine White) was used. This was a result of twenty dry MER-A basaltic rocks and soils. Using these values, an average K-value zone was created in these plots. The measured and simulated C/R ratios disagree when there is hydration or possible ALICs present in the sample. Thus, observed K-values of less than 0.91 indicate presence of ALICs.
5. Results

5.1 GUAPX Results

![GUAPX C/R vs. F(I) for Rock & Soil Classes](image)

Figure 9. Experimental C/R values extracted from GUAPX software plotted against F(I) for all selected rock and soil classes. The rock classes are depicted as filled, coloured shapes and soil classes as open, black shapes. Paso Robles are depicted as open squares. The linear trend line is constructed considering all the classes.

The GUAPX experimental C/R values plotted against F(I) reveals (Figure 9) Paso Robles, Independence, Gertrude Weise and Elizabeth Mahon classes as having a higher F(I) than the rest of the classes (> 45). Majority of the classes have a lower F(I), less than 44.5. Paso Robles class falls below the trend line. A similar pattern is seen for rock class Independence as well. Classes Gertrude Weise and Elizabeth Mahon fall above the trend line. All other classes fall within a 0.5 range of the average trend line.
5.2 K-value Results

The K-values plotted against F(I) for each rock and soil class reveals (Figure 10) a very distinct trend. Majority of the rock and soil classes contain lower F(I), below 44.5 while Paso Robles, Independence, Gertrude Weise and Elizabeth Mahon contain comparatively higher F(I). Most of the rock and soil classes also fall within or above the average K-value zone, including Independence. The K-values for Paso Robles falls significantly lower than the average 0.91 K-value, as expected. Gertrude Weise (filled, yellow triangles) and Elizabeth Mahon (open, black circles) also fall below the average K-value zone and show a similar trend to Paso Robles.

![K vs. F(I) for Rock & Soil Classes](image)
6. Discussion of Results

The rock and soil classes examined have been divided into groups A to E based on the similarity of results obtained after the K-value analyses for each of these classes.

6.1 Rock Classes

*Group-A: Adirondack, Algonquin, Backstay, Barnhill, Comanche, Clovis, Decartes, Halley, Irvine, Jibsheet, Methuselah, Montlava, Peace, Posey, Seminole, Torquas, Watchtower and Wishstone*

Background literature on these rock classes suggest at least some form of past aqueous alteration in their formation. Backstay class of rocks are high in K (0.89 wt%) and low in Fe (0.6 wt%), Mn and Cr. Due to their low Cl and Br concentrations, it is suggested that these rocks have undergone less alteration when compared to other rock classes (Bruckner et al., 2008; Hurowitz et al., 2006). Rocks in the Clovis class are enriched in P, S, Cl, Ti and Br. They are depleted in Ca and Cr. Their high S, Cl and Br content suggest that they were formed in some kind of an aqueous environment (Bruckner et al., 2008; Hurowitz et al., 2006). The Mosbauer instrument detected the presence of the mineral goethite in these rocks. This mineral forms only as a result of aqueous activity on Earth (Morris et al., 2006). They also have a high Ni content. It has been suggested that this indicates that these rocks could have formed as a result of a large meteorite impact. This impact may have released large amounts of heat and water which could have played a role in the alteration of these rocks (Bruckner et al., 2008). The rocks of Peace class, found near the Columbia Hills are high in Mg (13 wt%) and S (5.2 wt%). They contain the lowest concentrations of Al (1.5 wt%) and Si (17.5 wt%) of all the Gusev Crater rocks (Bruckner et al., 2008). The Br concentration in these rocks is enriched when compared to the Cl concentration. Since Br salts are more soluble than Cl, the researchers have suggested a past aqueous environment for their formation (Hurowitz et al., 2006). The rocks of the Watchtower class are high in P (2.3 wt%), K (0.5 wt%) and Ti (1.8 wt%) (Squyres et al., 2006). The Wishstone class rocks found near Husband Hill contain high concentrations of Na (3.7 wt%), Al (8 wt%), Ti (1.8 wt%) and Ca (6.4 wt%) (Hurowitz et al., 2006; Squyres et al., 2006). They are low in Mg (2.4 wt%), Fe (9 wt%) and Ni (50 ppm). The Mosbauer instrument detected the presence of around 1% ilmenite in these rocks (Ruff et al., 2006). Based on the mineralogy and chemistry of these rock classes, the K-value approach should indicate the possible presence of ALICs in these classes.
However, as seen in Figures 9 and 10, rock classes Adirondack, Algonquin, Backstay, Barnhill, Comanche, Clovis, Decartes, Halley, Irvine, Jibsheet, Methuselah, Montlava, Peace, Posey, Seminole, Torquas, Watchtower and Wishstone all have low fraction of invisibles F(I). All these classes fall within or above the calibration average K-value zone (0.87 to 0.95). Since there is very little to no deviation between the experimental and simulated C/R values or the K-values are close or above the average, invisible matter, like hydration is not present in these classes. The K-value analyses (Figure 11) for these classes fail to detect any possible ALICs. Also, when the K-values of these classes are compared to Paso Robles, they differ significantly. These classes do not follow a similar trend to Paso Robles, most of whose sample targets fall below the average K-value zone. Therefore, for these rock classes, the results of the K-value analyses is not in agreement with the literature’s suggestion of possible past aqueous activity in their formation.

**Group-B: Independence**

According to the literature, Independence class rocks are light-toned and rough in texture. They have a high Al (10 wt%) and low Fe (around 3.8 wt%) content, the lowest found thus far on Mars (Bruckner et al., 2008). The Mossbauer measurements indicated that one third of the Fe in these rocks is bound to ilmenite (Morris et al., 2008). They are highly altered rocks but may
contain some unaltered basaltic glass components. They are also enriched in Si, Ti, P, K and Ni and depleted in Mn, Mg and Cr (Arvidson et al., 2008). They are thought to contain smectite or smectite-like phases that were possibly formed as result of past aqueous alteration (Clarke et al., 2007). Based on these mineralogical and chemical suggestions, the results of the K-value analyses should indicate the possibility of the presence of ALICs in these rocks.

![K-value vs. F(I) for Group-B Rock Class](image)

**Figure 12.** K-value comparisons for Group-B rock class, Independence. The dashed line and the coloured zone represent the average K-value (calibration standard) with the error margins. The rock class is depicted as a filled, coloured shape. Paso Robles are depicted as open squares.

Independence class rocks do contain a higher F(I) as seen in Figure 9 and 10. They displayed a similar trend to Paso Robles in the GUAPX experimental C/R value plot (Figure 9). This indicated that they might contain possible ALICs since Paso Robles is a highly hydrated soil class. However, according to the K-value analyses (Figure 10 and 12), these rocks do not contain possible ALICs. This is because the samples fall above the k K-average. Also, they do not show a similar trend to Paso Robles. There is a discrepancy between the GUAPX results and K-value analyses for this class. However, the K-value approach is a more comprehensive technique. Therefore, the analysis for this class disagrees with the literature as it shows that Independence does not contain possible ALICs.

**Group-C: Elizabeth Mahon**

Based on the literature, Elizabeth Mahon is a highly altered rock class. It contains silica rich nodules (72 wt% Si) that are depleted in Fe (around 6 wt%) (Bruckner et al., 2008). They have a porous sponge-like texture where darker soil grains seem to be trapped within larger pores. They are presumed to have resulted due to aqueous leaching of basaltic precursors in an acid-rich
environment (Ruff et al., 2006). Therefore, the K-value analyses should indicate the presence of possible ALICs in these samples.

![K-value vs. F(I) for Group-C Rock Class](image)

**Figure 13.** K-value comparisons for Group-C rock class, Elizabeth Mahon. The dashed line and the coloured zone represent the average K-value (calibration standard) with the error margins. The rock class is depicted as a filled, coloured shape. Paso Robles are depicted as open squares.

Elizabeth Mahon contains comparatively higher F(I) than most other classes (Figure 9 and 10). These samples do not display a similar trend to Paso Robles in the GUAPX results (Figure 9). They are above the trend line while Paso Robles are beneath. However, the K-value plot (Figure 13) reveals that all samples in this class fall significantly below the K-value average. There is a significant deviation between the experimental and simulated C/R values and this indicates the presence of possible ALICs. The K-values of all samples in this class are lower than the K-average of 0.91. They also show a similar trend to Paso Robles, a class proven to be hydrated. This indicates that not only does this class possible contain ALICs but that they are in magnitudes as high as Paso Robles (6-18 wt% water) due to their similarly low K-values.

6.2 Soil Classes

*Group-D: Eileen Dean, Home Plate and Laguna*

Based on the literature, soil class Eileen Dean has a high SiO₂ concentration (50 wt% Si) (Ming et al., 2008). The soils are high in Mg and magnetite (Morris et al., 2008). Due to the enrichments in Ge, Cl and Zn, it has been suggested that these soils were altered by hydrothermal solutions rich in these elements. However, the PanCam did not reveal a hydration signature for this class. Laguna class soils are abundant in Ti, P, Mg, S, Fe and Cl and are depleted in Cr. They
are basaltic soils that may contain ilmenite \((Morris\ et\ al.,\ 2008)\). They occur quite frequently in the Gusev Crater region. They are rich in S, Cl and Br and the S is apparently associated with Mg in these soils. This mineralogy suggests that they had been mobilized by water in the past \((Wang\ et\ al.,\ 2006)\). To support the literature, the K-value analyses should indicate the presence of possible ALICs in these soils.

![Figure 14](image_url). K-value comparisons for Group-D soil classes, Eileen Dean, Laguna and Home Plate. The dashed line and the coloured zone represent the average K-value (calibration standard) with the error margins. The soil classes are depicted as open, black shapes. Paso Robles are depicted as open squares.

Majority of the samples within these classes contain low F(I) \((Figure\ 9\ and\ 10)\). They do not show a similar trend to Paso Robles in the GUAPX plot \((Figure\ 9)\). The k-values \((Figure\ 14)\) of all samples within these classes fall within or above the average K-value zone. Also, they fail to show a similar trend to Paso Robles, whose K-values fall below the K-average. Due to the lack to deviation between the experimental and simulated C/R values, these soil classes have higher K-values. Therefore, the K-value analyses indicate a lack of possible ALICs in these classes. This disagrees with the suggestions made based on their mineralogy and chemistry in the literature.

**Group-E: Gertrude Weise**

Literature proposes that Gertrude Weise soils are silica rich (upto 90 wt% Si) and high in TiO$_2$. The PanCam hydration signature for this class suggests persistent bound water in its silica structure \((Morris\ et\ al.,\ 2008)\). Also, the presence of opaline silica rich deposits have been proposed based on the spectral features. This is diagnostic as opaline silica deposits are usually produced in a hydrothermal setting \((Ruff\ et\ al.,\ 2011)\). So, the K-value analyses should indicate the possible presence of ALICs to support these mineralogical suggestions.
Gertrude Weise contains high F(I) (Figure 9 and 10) but do not show similar trends to Paso Robles in the GUAPX plot. However, the K-values of this class are well below the 0.91 average. Both the samples from this class fall below the average K-value zone and this deviation in the experimental and simulated C/R indicate the possible presence of ALICs. They also follow a very similar trend to Paso Robles (Figure 15). Therefore, the K-value approach indicated the possible presence of ALICs in these samples and a comparatively higher %hydration, similar in magnitude to Paso Robles.

7. Concluding Remarks

Objective: 1

Experimental C/R values extracted from GUAPX alone were not sufficient in showing possible ALICs. This is supported by the discrepancies seen in the case of classes Independence, Elizabeth Mahon and Gertrude Weise. The GUAPX results for these classes (Figure 16) show Independence below the trend line, along with Paso Robles (a known hydrated soil), Gertrude Weise and Elizabeth Mahon fall above the trend line and do not show a similar trend to Paso Robles.
These three classes yield different results in the K-value analyses (Figure 17). In contrast, Independence is above the average K-value zone and does not follow the Paso Robles trend. Therefore, it does not contain possible ALICs. Gertrude Weise and Elizabeth Mahon are below the average K-value zone and show a similar trend to Paso Robles even though they previously did not in the GUAPX plot.

This comparison provides conclusive evidence that the experimental C/R values extracted from the GUAPX software alone were not capable of indicating possible ALICs in the selected classes. This implies that further K-value analyses are needed to reveal the presence of possible ALICs in the classes.
Objective: 2

K-Value approach reveals significant levels of possible ALICs in Gertrude Weise and Elizabeth Mahon, comparable in magnitude to Paso Robles. The K-values for both these classes are lesser than the average 0.91 and fall below the average K-value zone (Figure 18). They also show a similar trend to Paso Robles.

![Figure 18. K-value comparison for classes containing possible ALICs; Gertrude Weise, and Elizabeth Mahon. The dashed line and the coloured zone represent the average K-value (calibration standard) with the error margins. Paso Robles are depicted as open squares.](image)

This is a significant find as these results show two previously unexamined Martian rock and soil classes to contain possible ALICs and in the same order of magnitude to Paso Robles (which contains 6-18 wt% water). This adds further evidence to the discovery of possibly hydrated rocks and soils on Mars that have undergone past aqueous alterations. Future research could be aimed at performing more simulations and calculating the wt% hydration or possible ALIC’s in these two rock and soil classes.
The K-value approach did not reveal possible ALICs for the other rock and soil classes examined, which is in disagreement with the literature. The literature suggested at least some degree of past aqueous alteration for most of the classes examined but the K-values of these classes fall within or above the average K-value zone (Figure 19). This disagreement could be a result of low levels of ALICs, lower than the detection limit. No fixed detection limit is known for MER-A ALICs but is assumed to be around 6-10 wt%. These classes might still be hydrated as the literature suggests but the wt% of ALICs could be below 6 wt% or below the detection limit. Also, the aqueous alteration process suggested by the literature may not have resulted in hydrated minerals with mineralogically bound water even though water may have played a role in their formation. These factors could result in the lack of detection of possible ALICs yet does not completely rule out the significance or presence of hydration in these classes. Further future research can be aimed at analysing these rock and soil classes even more extensively to uncover the reasons for this disagreement. Data from all MER-A instruments like PanCam, APXS, Mossbauer Spectrometer etc. can be combined to comprehensively re-examine the elemental compositions and mineralogy of the rock & soil classes that failed to show detectable levels of possible ALICs. Similar analyses can also be performed for all MER rock and soil classes for possible ALICs even ones that are suggested to be formed in alternate environments like geothermal or volcanic.

Figure 19. K-value comparison for possibly dry rock and soil classes that do not containing possible ALICs based on the K-value approach. The dashed line and the coloured zone represent the average K-value (calibration standard) with the error margins. The rock classes are depicted as filled, coloured shapes and soil classes as open, black shapes.
Acknowledgements

I offer profound thanks to Dr. J. L. Campbell and Glynis Perrett, for an opportunity to perform this project and for their valuable advice, direction and critiques throughout this project. I also thank Dr. R. Gellert for the use of MER-A spectra files, Dr. Susan Glasauer for initially recommending this project for MES research and Dr. Paul Sibley for accepting me into the MES program and allowing me to conduct an interdisciplinary research project. I acknowledge the School of Environmental Sciences, University of Guelph, NASA and the Jet Propulsion Laboratory for the use of their valuable data and/or equipment and computers.

Appendix

Master list of all MER-A Martian rock and soil classes (and sub-class(es)) extracted from numerous research papers. Rock and soil classes selected to be examined and analysed in this project are highlighted.

<table>
<thead>
<tr>
<th>Class</th>
<th>Sub-Class(es)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rock Classes</strong></td>
<td></td>
</tr>
<tr>
<td>Torquas</td>
<td>-</td>
</tr>
<tr>
<td>Wishstone</td>
<td>-</td>
</tr>
<tr>
<td>Watchtower</td>
<td>Watchtower, Keystone, Keel</td>
</tr>
<tr>
<td>Clovis</td>
<td>Clovis, Wooly Patch</td>
</tr>
<tr>
<td>Peace</td>
<td>-</td>
</tr>
<tr>
<td>Backstay</td>
<td>-</td>
</tr>
<tr>
<td>Adirondack</td>
<td>Adirondack, Joshua</td>
</tr>
<tr>
<td>Barnhill</td>
<td>Barnhill, Pesapallo</td>
</tr>
<tr>
<td>Irvine</td>
<td>-</td>
</tr>
<tr>
<td>Algonquin</td>
<td>Algonquin, Comanche</td>
</tr>
<tr>
<td>Independence</td>
<td>Independence, Assemblee</td>
</tr>
<tr>
<td>Descartes</td>
<td>-</td>
</tr>
<tr>
<td>Good Question</td>
<td>-</td>
</tr>
<tr>
<td>Everett</td>
<td>-</td>
</tr>
<tr>
<td>Montlava</td>
<td>-</td>
</tr>
<tr>
<td>Halley</td>
<td>Pot of Gold. Halley, Grahamland</td>
</tr>
<tr>
<td>Fuzzy Smith</td>
<td>-</td>
</tr>
<tr>
<td><strong>Elizabeth Mahon</strong></td>
<td>Elizabeth Mahon, Innocent Bystander</td>
</tr>
<tr>
<td>Plains Basalts</td>
<td>-</td>
</tr>
<tr>
<td>West Spur</td>
<td>-</td>
</tr>
<tr>
<td>Methuselah</td>
<td>-</td>
</tr>
<tr>
<td>Jibsheet</td>
<td>-</td>
</tr>
<tr>
<td>Seminole</td>
<td>-</td>
</tr>
<tr>
<td>Posey</td>
<td>-</td>
</tr>
<tr>
<td>Comanche</td>
<td>-</td>
</tr>
<tr>
<td>Stars</td>
<td>-</td>
</tr>
</tbody>
</table>
### Soil Classes

<table>
<thead>
<tr>
<th>Soil Class</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paso Robles</td>
<td>Paso Robles, Arad Samra, Arad Hula, Tyrone, Pasadena, Troy</td>
</tr>
<tr>
<td>Laguna</td>
<td>Panda, Liberty, Gobi, Boroughs, Doubloon</td>
</tr>
<tr>
<td>Gertrude Weise</td>
<td>-</td>
</tr>
<tr>
<td>Eileen Dean</td>
<td>-</td>
</tr>
<tr>
<td>Berry</td>
<td>Nougat, Moess Berry</td>
</tr>
<tr>
<td>Home Plate</td>
<td>-</td>
</tr>
</tbody>
</table>

### References


Catherine White, University of Guelph.


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