Expanding the Capability of the Alpha Particle X-ray Spectrometer Including Quantification of Fine-Scale Chemistry and Atmospheric Monitoring

by

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ABSTRACT

EXPANDING THE CAPABILITY OF THE ALPHA PARTICLE X-RAY SPECTROMETER INCLUDING QUANTIFICATION OF FINE-SCALE CHEMISTRY AND ATMOSPHERIC MONITORING

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University of Guelph, 2017

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The chemical composition of the surface of Mars has been investigated with the Alpha Particle X-Ray Spectrometer (APXS) dating back to the first Martian mobile explorer in 1997. The Alpha Proton X-Ray Spectrometer on the Sojourner rover predated the significantly improved Mars Exploration Rover (MER) APXS which flew on twin missions, each landing in 2004. The most recent and Canadian-built APXS, part of the Mars Science Laboratory (MSL) mission that landed in 2012, built on the experience of its MER predecessors and provides further design enhancements benefiting the mission’s science objectives. The APXS is perfectly suited for spaceflight through its use of $^{244}\text{Cm}$ sources to generate the alpha particles and X-rays required for X-ray spectroscopy. The complementary use of both particle-induced X-ray emission and X-ray fluorescence excitation methods provides the necessary level of sensitivity across the geologically relevant elements. The work presented herein focuses on three manuscripts and the associated unpublished work in their support that investigates the APXS method in detail to enhance the scientific return.

The longevity of the overall science mission offers a wealth of data for analysis across multiple landing sites on Mars. Though primarily used for solid samples, the APXS on the MER rover Opportunity has monitored the change in atmospheric argon density over six Mars years. The observed argon mixing ratio is consistent with previous published global climate models. Two short-lived spikes in argon density during the equatorial migration of the argon-enriched polar air mass are observed for the first time.

A novel analytical method is presented to deconvolve the endmember chemistry of surface features smaller than the dime-sized APXS field of view through a combined analysis of images and APXS data. The use of images in a new way facilitates the generation of a
three-dimensional operational environment for the APXS. The analysis method improves the interpretation of important APXS results in a constrained operational environment. Specific to the MSL mission primary objective, the method resolved chemistry at the sub-cm scale showing clear evidence of either multiple fluid events or an evolving fluid at some point on the surface of Mars.
Acknowledgements

I would like to start by thanking my parents, they have been an unbelievable support network and resource throughout my life. Their incredible patience answering the barrage of questions from my younger self undoubtedly fuelled my curiosity further to the point of pursuing higher education in physics. I also wish to express to the rest of my family and friends my gratitude for their unwavering support.

To past classmates with whom I’ve walked through the trenches of coursework, assignments, and testing, thank you for your different viewpoints, constructive debate, and contributions that furthered my understanding of the physical world. I also wish to thank the teachers and educators of various titles and disciplines for sharing your knowledge and wisdom throughout this journey. I owe gratitude as well to the many professors throughout my undergraduate and graduate degrees who have deepened and broadened my understanding of physics and were always available and supportive when questions arose. A very special thank you to Dr. Martin Williams and Dr. Joanne O’Meara whose enthusiasm in first year undergraduate physics lectures solidified physics as my discipline of choice more than a decade ago. I also wish to thank the entire physics department staff for their unbelievable support and jovial nature. A special thank you to Reggi Vallilee whose efforts are essential and often behind the scenes.

I would like to express my appreciation for the work and support of all the collaborators at institutions around the world with whom I’ve been privileged to work with and whose work, in some instances long before I started university, paved the way for the missions I’ve benefited from working on. Specifically to my APXS colleagues, you are an unbelievable team and it has been an honour and pleasure working and learning alongside you. I have benefited immensely from being a part of such a close-knit team of remarkable scientists and engineers and want to thank each of you for all you have done.

Finally, I wish to thank my advisory and examination committees. A special thank you to Dr. Rob Wickham for chairing the defence and providing peace of mind by handling the behind-the-scenes administrative duties. I would like to thank Dr. Denis Mücher for his helpful insights and viewpoints as someone who specializes in a related field. Gratitude to external examiner Dr. David Chettle for such a thorough analysis of this thesis - I am forever grateful for his comments and the wisdom he has shared. To Dr. Joanne O’Meara and Dr. Paul Garrett, thank you for all your support and guidance over the years. I was incredibly fortunate to have each of you on my committee and benefit from your experience and expertise. To Iain, I am humbled by how all of this started over a decade ago as an undergraduate student taking on a fourth year project in your class. Since that time you’ve been an unbelievable academic and personal support resource. I’m forever grateful for everything.

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Chapter 1

Introduction

1.1 Overview

The first mobile explorer landed on Mars in 1997 as part of the Mars Pathfinder (MPF) mission. The tiny rover, Sojourner, contained only cameras and a chemical analysis instrument, the Alpha Proton X-ray Spectrometer, a derivative of instruments flown on earlier Russian Vega and Phobos missions. The Alpha Proton X-ray Spectrometer provided the opportunity to analyze Mars rock and soil compositions for the first time [1].

Building on the success of MPF and its lessons learned, NASA returned to Mars with mobile explorers in January of 2004 by way of the Mars Exploration Rover (MER) mission. Spirit (MER-A, MER-2), landed at Gusev Crater, followed three weeks later by its twin, Opportunity (MER-B, MER-1), at Meridiani Planum [2, 3]. Each of these rovers were equipped with a suite of scientific instruments. Part of the Athena science payload of instruments on the MER rovers is the Alpha Particle X-ray Spectrometer (APXS) [4, 5]. The instrument offered significant performance upgrades to its Alpha Proton X-ray Spectrometer predecessor. The focus on the APXS was shifted from scattered alpha particles to X-rays, with the proton detection capability removed altogether [4]. The name of the instrument was changed to take advantage of the legacy and success of the Alpha Proton X-ray Spectrometer predecessor through the use of the same acronym [6]. Solar powered, each rover had a life expectancy of 90 Martian days (a Mars day is referred to as a sol - approximately 24 hours 40 minutes in duration) due to anticipated dust build up on the solar arrays [3]. However, wind-based solar array cleaning events were unpredicted and significantly extended the life
of the MER rovers [7]. Spirit was operational until complications arose after becoming stuck in soft regolith. The mission was terminated in 2010 [8]. Opportunity is still operational and is currently 4875 sols into a 90-sol mission as of 10 October 2017.

After the dissolution of the cosmochemistry and geochemistry departments at the Max Planck Institute in Germany, APXS technology and the MER APXS lead was recruited to Guelph. The most-recent mobile explorer sent to Mars, the Mars Science Laboratory (MSL) rover Curiosity, landed in August of 2012. Equipped with a state-of-the-art instrument suite and sent to seek out past habitable environments on Mars, MSL requires ample and more stable power, provided by a $^{238}$Pu radioisotope thermoelectric generator [9]. The MSL rover scientific payload also contains an APXS, significantly improved on the success of MER making it a third-generation APXS instrument and the fourth to study the composition of the surface of Mars [10].

Contained herein are published (§2) and submitted (§3) manuscripts presenting work expanding the APXS method and improving the results obtained through measurements conducted on the surface of Mars. These manuscripts are preceded by the necessary introductory information - including theory and a more-detailed discussion of the MER and MSL instruments and operation - and followed by current unpublished work (§4) either planned for publication or conducted in support of the presented publications but not contained within.

1.2 The APXS Instrument

The APXS combines the complementary principles of particle-induced X-ray emission (PIXE, §1.2.3.3) and X-ray fluorescence (XRF, §1.2.3.1) to interrogate a sample [4, 5, 11]. Utilizing the alpha decay of the $^{244}$Cm sources and the resulting X-ray emissions by Pu daughter nuclei, the APXS benefits from the low-Z sensitivity of PIXE combined with the high-Z sensitivity of XRF, resulting in a greater sensitivity for characteristic lines in the 0.5-25 keV range than either excitation method alone (see Figure 1.1). This section will discuss both the similarities and differences in the APXS instrument on both MER (§1.2.1) and MSL (§1.2.2).
Figure 1.1: Spectrum of laboratory sample SSK measured with the MER APXS (blue) and with the MER APXS with PIXE suppressed (red). Figure replicated from [4]. Traditional XRF measurements, conducted with X-ray tubes, are prone to a higher low-energy background due to bremsstrahlung radiation (see §1.3.2.3).

1.2.1 MER APXS Configuration

The MER instrument sensor head consists of six alpha particle detectors surrounding six $^{244}$Cm sources around a central X-ray detector, in addition to the necessary electronics as illustrated in Figure 1.2. There is a minimum $\sim 3$ cm gap between the instrument face and the opening for sample analysis which has doors that can be closed. For calibration purposes, the MER APXS copper-beryllium doors have thin layers of Kapton and gold [4]. The MER APXS circular field of view (FOV) opening angle is approximately 60$^\circ$ for the X-ray mode, resulting in a FOV diameter of approximately 3.5 cm if deployed to contact.

The MER electronics have a signal processing time of roughly 300 $\mu$s [4]. Typical background elements in a spectrum consist of Zr (collimator), Cu (mounting screw) and Ti (foils). It should be noted, that the MER-A and MER-B APXS instruments have slightly different detector response functions due to differing foil and Be window thicknesses [5]. There are also differences in the active area and thickness of their detectors. In general, a typical X-ray spectrum has a count rate of 60 to 70 counts per second (cps), decreasing with source activity and instrument standoff (see Figure 2.13 for the MSL curve - analogous to MER).
An atmospheric X-ray spectrum produces under 3 cps. Alpha spectra typically produce under 4 cps on solid targets and under 1 cps for atmospheric measurements.

1.2.1.1 Sources

On MER, the central X-ray detector is surrounded by six $^{244}\text{Cm}$ sources. The sources have a thin (on the order of 2-5 microns thick [4]) titanium foil as an exit window to prevent sputtering of the radioactive curium onto the sample [4]. This in turn attenuates the alphas (alpha particles) from 5.8 MeV to roughly 5.2 MeV, also avoiding a 5.7 MeV $^{12}\text{C}(\alpha,\alpha')^{12}\text{C}$ resonance that would arise ubiquitously from interactions with the 95%+ CO$_2$ Martian atmosphere, overwhelming any trace signal of carbon local to the surface [4, 12, 13]. There is, additionally, a resonance at approximately 3 MeV for oxygen; however, this is not a concern as scattered alphas at 3 MeV would not have enough energy to be detected [12]. There is also a 4.25 MeV alpha elastic scatter resonance for carbon [14], explaining the approximately two-fold elevation in C-peak area in atmospheric alpha spectra previously.
The six radioactive $^{244}$Cm sources had a source activity at landing of roughly 1.1 GBq. Curium-244 decays to $^{240}$Pu via alpha emission (two lines at approximately 5.8 MeV) [4, 5, 11]. Roughly 23% of all decays result in an excited state of $^{240}$Pu, potentially relaxing via the release of a Pu characteristic X-ray (primarily 14 and 18 keV), yielding an approximate 10:1 alpha:X-ray generation ratio [4, 5]. In addition to alpha and X-ray emission, $^{244}$Cm can also decay via spontaneous fission, releasing a neutron of $\sim$MeV energy [15]. Spontaneous fission occurs in roughly 0.00014% of decays. However, given the activity of the MER $^{244}$Cm sources, this results in roughly 1500 neutrons emitted over $4\pi$ per second. Neutrons are deeply penetrating due to the lack of Coulomb repulsion and can damage the X-ray detector with time. $^{244}$Cm also emits 42.8 keV $\gamma$-rays with a relative intensity of 0.02% [4]. The low $\gamma$-intensity is crucial for a weak background.

In addition to both alpha and X-ray production, $^{244}$Cm possesses other benefits of significant importance for an instrument bound for space flight. Curium-244 has a long half-life (over 18 years [16]) providing sufficient source activity well into lengthy missions. Space-bound instruments are limited in size, weight, power consumption, and data volume produced [17]. Radioactive sources, especially $^{244}$Cm due to its high specific activity, offer a significant weight reduction and are more robust than X-ray tubes - critical when considering the hazards of delivery to, and operation on, another planet. Furthermore, X-ray tubes require considerable power to generate X-rays whereas radioactive sources are continually emitting without any associated power demand.

1.2.1.2 Detectors

The MER APXS utilizes a single silicon drift detector (SDD) for X-ray detection. Complementary RBS alpha detectors are external to the sources surrounding the central X-ray detector (Figure 1.2). The alpha detectors have a second identical ring of detectors directly behind, not exposed to any alpha particles but detecting rather the high-energy $\gamma$-ray background to the foreground alpha detectors. This permits, in theory, the removal of alpha spectra background [4, 5]. Due to a firmware bug in both the alpha and background data acquisition modes, this is not directly possible [12].
The MER X-ray SDD detector has an active area of 10 mm$^2$ and a 5 $\mu$m Be window achieving a resolution of 160 eV at 5.9 keV [4]. The alpha detectors have collimators, made from machined stainless steel into honeycomb orifices, and are most likely windowless CCD (charge couple device) detectors, similar to SDDs, and are light sensitive [4, 5]. Light sensitivity can cause dead time issues when conducting atmospheric measurements that commence prior to sunset [4], discussed further in §3.

1.2.1.3 Data Products

The MER APXS can acquire up to 12 individual measurements within a single integration. These 12 measurements are stored in the battery-buffered APXS memory. Whenever a new measurement is acquired, be it during the pre-determined duration of a given measurement within one integration or a new integration altogether, the oldest measurement is purged from the memory buffer and each measurement is incremented into an older memory slot. Each of the 12 measurements are 2.5 Kbytes in size. A 2 Kbyte structure corresponding to engineering data follows (see Table 1.4). A single MER APXS data product is a mere 32 Kbytes. Within each of the 12 measurements are 1024 bytes of X-ray data (see Table 1.1), 512 bytes of alpha particle data (see Table 1.2), 512 bytes of background data (see Table 1.3), and 512 bytes of temperature data. The 512 channels on the X-ray data limits the upper energy range to around 15 keV. The lower-energy threshold was intended to be well-below sodium (roughly 1 keV). However, upon integration into the rovers it was determined that the induced capacitance of the cabling adjusted the lower-energy limit to roughly that of the sodium peak. Thus, the sodium peak on MER is calculated by fitting the half that is visible in the spectrum. A more-detailed discussion of the MER APXS data structure can be found in [18].

<table>
<thead>
<tr>
<th>Channels</th>
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<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1-2</td>
<td>Lifetime in units of 10 seconds. 16-bit LSB first uint.</td>
</tr>
<tr>
<td>1</td>
<td>3-4</td>
<td>Spectrum identifier. 12-bit LSB first uint.</td>
</tr>
<tr>
<td>2</td>
<td>5-6</td>
<td>A0 (multiplier for the gain). 16-bit MSB first uint.</td>
</tr>
<tr>
<td>4 - 510</td>
<td>9-1022</td>
<td>Counts. 16-bit LSB first uint.</td>
</tr>
<tr>
<td>511</td>
<td>1023-1024</td>
<td>Overflow counts. 16-bit LSB first uint.</td>
</tr>
</tbody>
</table>
Table 1.2: Binary data structure of MER APXS Alpha spectra.

<table>
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<th>Channels</th>
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<td>0</td>
<td>1025-1026</td>
<td>Lifetime in units of 10 seconds. 16-bit LSB first uint.</td>
</tr>
<tr>
<td>1</td>
<td>1027-1028</td>
<td>Spectrum identifier. 12-bit LSB first uint.</td>
</tr>
<tr>
<td>2</td>
<td>1029-1030</td>
<td>A0 (multiplier for the gain). 16-bit MSB first uint.</td>
</tr>
<tr>
<td>4 - 254</td>
<td>1033-1534</td>
<td>Counts. 16-bit LSB first uint.</td>
</tr>
<tr>
<td>255</td>
<td>1535-1536</td>
<td>Overflow counts. 16-bit LSB first uint.</td>
</tr>
</tbody>
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Table 1.3: Binary data structure of MER APXS Background spectra.

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</tr>
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<td>0</td>
<td>1537-1538</td>
<td>Lifetime in units of 10 seconds. 16-bit LSB first uint.</td>
</tr>
<tr>
<td>1</td>
<td>1539-1540</td>
<td>Spectrum identifier. 12-bit LSB first uint.</td>
</tr>
<tr>
<td>2</td>
<td>1541-1542</td>
<td>A0 (multiplier for the gain). 16-bit MSB first uint.</td>
</tr>
<tr>
<td>4 - 254</td>
<td>1545-2046</td>
<td>Counts. 16-bit LSB first uint.</td>
</tr>
<tr>
<td>255</td>
<td>2047-2048</td>
<td>Overflow counts. 16-bit LSB first uint.</td>
</tr>
</tbody>
</table>

Temperature data are acquired every 30 seconds. There are 256 channels (0 - 255) corresponding to bytes 2049-2560 in pairs of 8-bit unsigned integers (uint). Warm electronic box temperature is contained in the first byte, sensor head temperature is contained in the second byte. These temperature data are used for internal adjustments of temperature-sensitive instrument parameters. Temperature values are multiplied by 1.442 to convert to Kelvin.

Table 1.4: Binary data structure of MER APXS engineering data.

<table>
<thead>
<tr>
<th>Bytes</th>
<th>Description</th>
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<tbody>
<tr>
<td>1-2</td>
<td>A0 TC (X-ray) 16-bit MSB first uint</td>
</tr>
<tr>
<td>3-4</td>
<td>G TC (X-ray) 16-bit MSB first uint</td>
</tr>
<tr>
<td>5-6</td>
<td>A0 TC (Alpha) 16-bit MSB first uint</td>
</tr>
<tr>
<td>7-8</td>
<td>G TC (Alpha) 16-bit MSB first uint</td>
</tr>
<tr>
<td>9-10</td>
<td>A0 TC (Background) 16-bit MSB first uint</td>
</tr>
<tr>
<td>11-12</td>
<td>G TC (Background) 16-bit MSB first uint</td>
</tr>
<tr>
<td>13</td>
<td>Cycle interval/min. uint</td>
</tr>
<tr>
<td>14</td>
<td>Spare byte, adjustable, not used</td>
</tr>
<tr>
<td>15-23</td>
<td>Reserved bytes (9 bytes)</td>
</tr>
<tr>
<td>24-25</td>
<td>Uptime from the last power up or software reset/10s. (16-bit LSB first uint)</td>
</tr>
<tr>
<td>26-31</td>
<td>Reserved bytes (6 bytes)</td>
</tr>
<tr>
<td>32-33</td>
<td>Address of the last command written into the logbook</td>
</tr>
<tr>
<td>34-254</td>
<td>Reserved bytes, (221 bytes)</td>
</tr>
<tr>
<td>255-2048</td>
<td>Circular written log book of received command bytes.</td>
</tr>
</tbody>
</table>
1.2.2 MSL APXS Configuration

By abandoning alpha detectors, the MSL APXS sensor head is more compact than its MER predecessor, permitting bringing the sources and detector into closer proximity with the sample and thus increasing the obtained spectral count rate by about a factor of three [17]. The sensor head is mounted on the rover’s Robotic Arm (RA) component of the MSL Sample Acquisition - Sample Processing and Handling (SA/SPaH) tools suite (see Figure 2.14) while the electronics are mounted in the Rover Chassis. An onboard calibration target is accessible for post-landing calibration [19]. There is also an observation tray where the rover can deposit fine samples for APXS analyzes [19, 20]. The MSL APXS instrument is illustrated in Figure 1.3 and shown deployed on the surface of Mars in Figure 2.14.

![Figure 1.3: Images of the MSL APXS. Contact sensor (grey, rectangular, front face), detector (centre) and sources (surrounding detector, open sources silver and shiny, closed sources smaller and matte grey) visible in centre and upper-left image. Images acquired by the Mastcam camera on Curiosity. Image credits: NASA/JPL/MSSS.](image)

Unlike MER where contact with a sample surface is used to open the instrument doors [4], the MSL APXS is routinely deployed to contact the sample surface when possible commensurate with instrument safety. Contact with the surface is determined by a contact-sensing
plate [21, 22]. The MSL APXS also offers the ability to use “proximity mode” to deploy the APXS and the arm-mounted Mars Hand Lens Imager (MAHLI) camera close to the surface without contacting potentially dangerous unconsolidated material such as soil. A more detailed discussion of proximity mode can be found in §2.2. The circular APXS FOV on MSL is constrained by a $\sim 45^\circ$ opening angle, resulting in a circular FOV 15 mm in diameter when deployed to contact [21, 22]. Count rates with the MSL APXS can exceed 300 cps, decreasing with source activity and instrument standoff.

1.2.2.1 Sources

On MSL, the alpha detectors were removed as the instrument is purely focused on X-ray detection. The increased energy range on MSL, with an upper limit of approximately 25 keV compared to 16 keV on MER, permits the additional observation of incoherent and coherent scattered Pu L lines, primarily at 18.3 (L$_{\beta_1}$) keV as illustrated in Figure 1.4. Lower intensity lines do exist and contribute to the spectral background including, for example, the Pu M-lines that overlap the Ca K$\alpha$ peak.

Six $^{244}$Cm sources are either covered by titanium foils (open, silver and shiny in Figure 1.3 top-left and centre) or by beryllium (closed, grey and matte in Figure 1.3 top-left and centre), alternating in order to provide axial symmetry. Open sources emit both alpha particles and X-rays whereas closed sources fully absorb alphas and only emit X-rays. The use of both open and closed sources results in a sensitivity curve that is more balanced between PIXE (low-Z) and XRF (high-Z) across the energy range of a spectrum. Specifically, the alpha source activity was maintained by doubling the thickness of the open sources compared to MER but reducing from 6 to 3 alpha emitters. The closed sources increase the high-Z count rate, improving the detectability of trace elements [10, 17]. Careful concern should be given to the increased background associated with increasing the X-ray counts as this could offset the intended goal. The total source activity for the MSL APXS at landing was approximately 2 times that of MER at landing.
1.2.2.2 Detectors

The MSL APXS also utilizes a SDD X-ray detector with an improved resolution of 140 eV at 5.9 keV compared to 160 eV for MER. The MSL APXS SDD is also situated in the centre of the instrument face as illustrated in Figure 1.3. The detector contains a beryllium window and also a Peltier cooler that improves spectral resolution during the warmer periods of the diurnal (and yearly) Mars temperature cycle. The MSL APXS is not equipped with alpha or background detectors like its MER predecessor [10, 17].

1.2.2.3 Data Products

The MSL APXS can acquire up to 13 individual measurements within a single integration, one more than MER. Unlike MER, contents of a measurement are not saved onboard the APXS after transmission to the rover, resulting in 13 empty measurement banks every time the instrument is powered on. Similar to MER operations, the rover may sleep to conserve energy after starting the APXS and must again power on to stop the integration and retrieve the acquired data. Each data product is processed into spectra that consist of 1024 channels of temperature-compensated X-ray spectra. Relevant engineering data once again occupy the first few channels of a spectrum. Live time is expressed in seconds. The lower energy...
threshold is below the sodium peak, at around 700 eV, while the upper energy limit has been increased to approximately 25 keV in order to observe more incoherent and coherent Pu lines.

A MSL APXS data product consists of 29818 bytes of data. A given channel of MSL APXS data is stored as a 16 bit value. Due to the potentially high count rates combined with long integration times, some channels may exceed the 16 bit count maximum (65535) during an individual measurement, thus counting up from 0 again. This is carefully corrected by the MSL APXS data processing tools. A more-detailed discussion of the MSL APXS data structure, including specifics similar to those presented in §1.2.1, can be found in [19].

1.2.3 The APXS Method

1.2.3.1 X-ray Fluorescence

X-ray fluorescence describes the ionization of atoms using electromagnetic radiation (in the X-ray wavelength) and the consequent emission of a characteristic X-ray during the relaxation of an ionized atom from the induced excited state. The emitted X-ray has a characteristic energy corresponding to the electron transition experienced during relaxation. Upon ionization, there are several competing methods for relaxation including radiationless relaxation. Incident X-rays can be scattered coherently (elastically, Rayleigh) or incoherently (inelastically, Compton). Non-ionization interactions with the electron cloud (bound electrons) result in elastic collisions while non-ionization interactions with free electrons result in inelastic collisions, reducing the energy of the impinging X-ray [23]. Photon scattering is discussed further in §1.2.3.2.

Beer-Lambert law (utilized in §4.1) describes the relative intensity of X-rays at a depth $x$ within a sample as

$$
\frac{I}{I_0} = e^{-\mu_L x}
$$

(1.1)

where $\mu_L$ is the linear attenuation coefficient, a property of the target equal to the product of the mass attenuation coefficient, $\mu$, and the density, $\rho$. Attenuation coefficients generally decrease with increasing energy. When dealing with a compound, linear additivity of mass
...attenuation coefficients applies.

Whether ionized by incident X-ray radiation in the case of XRF, or charged particles in the case of PIXE (§1.2.3.3), atoms relax primarily from an excited state via three not-mutually-exclusive methods:

1. emission of a characteristic X-ray,

2. emission of an Auger electron, or

3. a Coster-Kronig transition.

Of the above points, characteristic X-rays and Auger electrons are in direct competition. For example, when a vacancy is generated in the K-shell, the atom is in an ionized and excited state. To relax, an electron transitions from an upper shell (e.g. L-shell) and releases energy to do so. The released energy can be in the form of an X-ray and/or via another electron ejected kinetically. For an emitted characteristic X-ray, the energy is specific to the transition energy of the element (e.g. K\(_{\alpha}\) line from a L-K transition) [23].

Auger electron emission is a radiationless process whereby an electron is emitted instead of a characteristic X-ray. The competing Auger and photoelectric processes dominate in different regimes. Below Z=32 (Ge), Auger dominates while above fluorescence dominates. Coster-Kronig transitions occur between electrons in the same shell (i.e. L\(_3\) to L\(_1\)), are radiationless, and can be considered a special case of the Auger process [23].

Electron transitions have specific classifications. A transition from the L-shell to the K-shell is denoted by K\(_{\alpha}\) whereas from the M-shell to the K-shell is a K\(_{\beta}\) transition. There are further classifications for K\(_{\alpha 1}\) and K\(_{\alpha 2}\) based on specific transitions. K\(_{\alpha}\) and K\(_{\beta}\) lines have relative intensities of a known ratio that varies from element to element. Deviation from this ratio can provide insight into possible absorbers between the two energies. The energy separation between K\(_{\alpha}\) and K\(_{\beta}\) lines increases with Z [23]. At low-Z it is sufficient to model the K\(_{\alpha}\) and K\(_{\beta}\) lines as one peak. As Z increases, modelling with a single peak leads to considerable error even before the two peaks are clearly distinct.

Absorption cross-sections increase with \(Z^{4.5}\), or, more specifically, increase with \(Z^4\) at low energy and \(Z^5\) at high energy. For comparison, \(\sigma_R\), the cross-section for Rayleigh...
scattering, scales with $Z^2$ and $\sigma_C$, the cross-section of for Compton scattering, scales with $Z$. Absorption cross-sections have a geometrical component and increase with target atomic number. Absorption edges arise when photon energies are below that of the binding energy of a shell, resulting in a steep drop in absorption cross-section [23].

### 1.2.3.2 Compton and Rayleigh Scattering

Compton scattering is the inelastic scattering of electromagnetic radiation with electrons that results in a change in direction and reduction in energy for the incident photon. Compton interactions are typically with the outer shell and loosely bound or free electrons. Compton scattering favours low-$Z$ elements [23].

The energy transfer during a Compton scattering event is given by

$$\frac{E_C}{E_{C0}} = \frac{1}{1 + \frac{E_{C0}}{E_e}(1 - \cos \theta)}$$

where $E_C$ the energy of the Compton-scattered photon after the interaction, $E_{C0}$ is the energy before the interaction, and $E_e$ is the rest mass energy of an electron (0.511 MeV). Compton scattering heavily favours forward scattering, with low yield at high angles, resulting in only a factor of 2 difference between $\theta = 90^\circ$ and $\theta = 180^\circ$.

Rayleigh scattering is the elastic scatter of electromagnetic radiation resulting in a change in direction but not energy of the incident radiation. These interactions are typically on the tightly bound and rigid inner-shell electrons, in addition to the nucleus themselves, that leave the atom neither ionized nor excited. Since EM radiation does not respond to electric fields, the Coulomb potential of an atom is not relevant. Rayleigh scattering favours high-$Z$ elements [23].

### 1.2.3.3 Particle-Induced X-ray Emission

Particle-induced X-ray emission (PIXE) follows a similar overall pathway to characteristic X-ray emission as XRF, instead using charged particles as a means of target atom ionization. Charged particles interact differently with matter than X-rays. Shallower penetration depths lead to PIXE analyzes focusing on the surface of a sample while XRF obtains chemistry from
When ionizing with heavy charged particles, like alpha particles, the ability to ionize falls off rapidly with target Z, roughly as $Z^{-4}$. Considering sample depth, most ionization events are produced near the surface. As depth increases, the fraction of total ionization events per unit volume decrease to zero. From the detection perspective, attenuation of the emitted X-rays results in further skewing to shallow penetration depths. As sampling depth is increased, secondary attenuation becomes increasingly important as the number of interactions scales with depth [24].

1.2.3.4 Sample Matrix Effects

Fluorescence of a given element is achieved through ionization by either photons or charged particles. Ionization by photons occurs so long as the photon energy is greater than the binding energy of the shell. However, the ionizing photons need not be directly from the instrument photon source. Fluorescent characteristic lines are attenuated by lower-energy transitions. The K-line of a low-Z element like oxygen and the L-line of iron are both strong absorbers that are prominent in geological samples both on Earth and Mars. Enhancement is largest for K-lines close to the high-energy side of an absorption edge of a lower-E line. Typically, the best absorber is 2 or 3 atomic numbers below the X-ray characteristic energy. The 0.7 keV L-lines of iron attenuate twice as much as the K-lines of oxygen at 0.5 keV in the low-energy range, relevant especially to 1 keV Na X-rays. Ni in Fe-Ni meteorites is $\sim 3$ times more absorbed than in a sample with average Mars composition. The absorption of a secondary photon or scattered photon is typically ignored as it is a minor effect [4, 5, 23, 24].

1.3 Detectors

Radiation detectors, like lithium-drifted silicon (SiLi) detectors and SDDs, operate by converting the energy of an incident photon into a proportional voltage. The electrons liberated from the silicon crystal lattice during the cascade caused by the initial photon interaction are swept away by an electric field and integrated into a total charge that is proportional to the energy. This charge is ultimately converted into a voltage, and, through calibration of
photons of known energy, the voltage is converted to the energy of the detected photon [25].

Detectors are considered to have three layers. The top-most layer encountered by a photon is a thin dead layer where the crystal structure is flawed due to interactions with the environment resulting in no charge collection by the device. Below is a transition from the dead to active layer where there is partial charge collection. Finally the active layer (or depletion zone) is encountered where complete charge collection efficiency is obtained. The active layer is depleted of its free electrons via a reverse bias voltage. The voltage generates an electric field, sweeping away all electrons to a transistor. Any constant current, absent ionizing photons, can be attributed to thermal leakage of charge carriers excited above the band gap, reduced by cooling the unit [25]. A discussion of APXS signal processing can be found in [5].

The charge itself is generated by an incident photon. The photon will be absorbed by the silicon crystal structure of the detector. In the active layer, this will emit either an Auger electron or characteristic Si X-ray; the former is more probable. Once an Auger electron is emitted, the electron can ionize a silicon atom once again resulting in more electrons until the cascade concludes, typically, after a few picoseconds. These liberated electrons are collected by the reverse bias voltage. While a signal is being processed, the detector is “off” in regards to further integration of charge, referred to as “dead time” [25]. Incomplete charge collection is discussed in §1.3.1.4. In addition to incomplete charge collection, ambiguity can arise due to detector artifact satellite peaks, discussed in §1.3.2.4. All detectors are unique due to geometry and electronics. Typically, there exists a gas between an entrance window to the detector (normally a beryllium window, see §1.3.1.3).

The penetration depth in silicon for X-rays of interest to the APXS (0.5-25 keV) is from \(\sim0.4-\sim1900 \mu m\). Detectors can be constructed quite thin as a result, decreasing noise but reducing efficiency for higher energy events. Thin detectors can absorb high-energy photons due to Compton scattering within the detector. X-ray attenuation is most likely to be near the surface according to Beer’s law (Equation 1.1). Electrons can only occupy specific bands in the structure of a semiconductor. The highest band, the conduction band, is partially filled. Lower is the valence band which is bound and full. The difference is referred to as the band gap. Radiation can induce a transition from valence (bound) to conduction (unbound)
if the energy is large enough to liberate the electron across the band gap. When this happens, 
the electron is then free to move and eventually be collected and integrated by the detector 
electronics. Temperature affects the population states within the valence and conduction 
band. Reducing temperature lowers the frequency of thermal-induced electrons moving from 
the valence to conduction band which presents as thermal noise. Occasionally neutrons will 
interact and damage the silicon crystal structure of the detector. This displacement damage 
leads to an increase in thermal noise presenting as an increase in FWHM over time at a 
given temperature. The rate of FWHM increase at a given temperature slows over time. 
Figure 1.5 illustrates detector degradation over time measured by the MSL instrument.

![Graph showing FWHM vs Temperature]

**Figure 1.5**: FWHM achieved for MSL spectra for integration-averaged temperatures ranging 
from -77°C to 8°C. Data points highlighted in red were measured between -8°C and -9°C on 
the specified sol illustrating the increase in FWHM observed over time at a set temperature. 
FWHM “hump” at ~-50°C corresponds to MSL Peltier cooler on/off temperature.

1.3.1 Properties of Detectors

1.3.1.1 Detector Resolution

A detector’s resolution is conventionally defined by the full-width at half-maximum (FWHM) 
at 5.9 keV, corresponding to the Mn $K_{\alpha}$ line, easily visible when using $^{55}$Fe sources. The
broadness of a peak is the result of a combination of electronic and detector noise given by

\[ \text{FWHM} = \sqrt{\Delta E_{\text{DET}}^2 + \Delta E_{\text{ELEC}}^2}. \] (1.3)

Electronic noise arises from detector dimensions and signal processing. Reducing detector area and thickness decreases electronic noise and thus results in more-resolved peaks. Thermal leakage currents create a fluctuating background that is read by the pulse shaper. When charge is collected, the pulse shaper defines the amplitude with respect to this background, resulting in statistical fluctuations about a varying mean, producing a broader peak. Thermal noise can be reduced by cooling the unit. Deviation towards better resolution than dictated by Poisson statistics is described by the Fano Factor (§1.3.1.2), given by

\[ \Delta E_{\text{DET}}^2 = 2.35^2 E \epsilon F \]

where \( E \) is energy, \( \epsilon \) is energy required to produce an electron-hole pair (\( E/\epsilon \) is pairs produced) and \( F \) is Fano Factor. The scale factor of 2.35 arises from the conversion of standard deviation (\( \sigma \)) to FWHM. \( \Delta E_{\text{DET}} \) dominates higher energy (10s of keV and above) whereas \( \Delta E_{\text{ELEC}} \) dominates lower energy [25].

**1.3.1.2 Fano Factor**

The Fano factor is a result of non-independent processes within the detector. The number of interactions that arises due to an ionization event varies, however, the energy lost does not. This results in a reduction in the electronic component of noise as typical Fano factors are around 0.1. The Fano factor is a function of material but varies from detector to detector. Variations with energy and temperature remain debated [25].

An analogy of the Fano factor is given by what is described as “crazy carpentry”. Consider a board of length \( L \) in units of ionization events. An ionization event is created resulting in a cut of width 1 at some position \( x \) on the board. This results in two pieces of board, \( x \) and \( L - x - 1 \). Random cuts continue to be made. Eventually, boards become shorter than 1 and are discarded (dissipated) as waste. Eventually, all the remaining boards are less than
1 unit length. Clearly, the number of cuts made is proportional to the starting length, $L$, but will produce a waste of boards shorter in length than 1. If we consider each cut to be an ionized electron, the total number of ionizations is given by $n_0 < E_0/1$. Thus, if $y$ is the yield, we have $n_0 = yE_0$. The average energy required to ionize an electron, $\omega = 1/y$, gives the relation $n_0 = E_0/\omega$. The Fano factor is then determined by

$$F = \frac{\langle n_0 \rangle^2}{n_0}$$

where $\langle n_0 \rangle^2$ is the variance of $n_0$. This provides an interesting result as $\omega$ and $F$ can both be determined mechanically independent of physics [25].

1.3.1.3 Beryllium Window

The detector window protects the detector from low-energy photons, such as visible light, which would result in an inflated low-energy count rate and lead to an increase in dead time within a spectrum. The window is typically made of a low-Z material like beryllium ($Z=4$) to prevent characteristic lines from the window material appearing in the spectrum. The beryllium window does not stop neutrons from damaging the detector but keeps moisture from coming into contact with the detector, especially important when actively cooled by a thermoelectric cooler.

1.3.1.4 Incomplete Charge Collection

Incomplete charge collection (ICC) occurs when charge generated from an ionization event is lost [25]. An analogy is given by dropping an object (e.g. coin) into a carbonated beverage. The amount of bubbles produced depends on the height it was dropped from. Tabulating all the bubbles that reach the surface offers a gauge of height. Problems arise when bubbles get stuck to the walls or dissipate while rising. Additionally, any constant bubble stream will appear as a background, much like leakage current.

Incomplete charge collection manifests in peaks of non-Gaussian shape. The result is modelled by a hypermet function [26]. Surface dead layers or imperfections are one source of ICC. Secondary electrons, Auger or photoelectric, as well as secondary photons can escape
from the active zone. Along the periphery of the detector, charge collection is prone to edge effects due to a reduced electric field and also physical escaping to the detector shroud material; these can be reduced by collimation which constrains the incident photons to a narrow beam directed at the centre of the detector. Lost energy in the form of phonons contributes to ICC as well [25].

### 1.3.2 Detector Response Function

The hypermet function consists of a convolution of a Gaussian function with exponential tails on the low-energy side of the peak and a flat shelf from the K-shell binding energy through to the low energy limit of a spectrum. Deviations from pure-Gaussian are the result of interactions within dead layers, detector contacts, the detector window, backings, sidewall coatings, and surface layers [26, 27]. Peak broadening is a result of the processes discussed in §1.3.1.1. A detailed description of the hypermet function, including presentation of equations, can be found in §4.2.2.

#### 1.3.2.1 Exponential Tailing

Exponential tails represent small fractions of the total charge that is lost at the end of a cascade. This is typically due to bulk trapping during the drift of carriers to the electrodes or the diffusion of charge from the active zone prior to collection by the field. The tail intensity (area) in relation to peak area drops smoothly with energy while tailing broadens smoothly with increased energy due to more interactions occurring at higher energy thus inducing more ICC [25, 27].

#### 1.3.2.2 Shelf

When high-energy electrons escape at the start of a cascade, it leads to a shelf-like background below the photopake. At high energies, Compton scattering will also contribute [27]. The shelf is typically of amplitude $\leq 1\%$ of the primary peak height.
1.3.2.3 Background

The background of a spectrum must be properly subtracted for proper quantification of peak areas. If the background is large compared to the signal investigated, it can severely hamper the ability to resolve trace signals. When ionizing with charged particles, bremsstrahlung radiation can be a major source of background. Bremsstrahlung radiation occurs when the incident charged particles lose energy passing through a Coulomb field. These interactions result in the particle changing energy/velocity and in turn emitting a continuum of X-rays [24, 28]. The probability of bremsstrahlung is proportional to:

\[ P_B \propto \frac{q_p^2 Z_i^2 T_p}{M_p^2} \]  \hspace{1cm} (1.4)

where \( q_p \) is the projectile’s charge and \( T_p \) is its kinetic energy.

Bremsstrahlung is dominant when using electrons as the ionization method. As a rough order-of-magnitude comparison, ionizing by protons results in a decrease in bremsstrahlung background of roughly 6 orders of magnitude due to the increase in mass compared to ionization by electrons. The increase in charge of an alpha particle is offset by its increase in mass, resulting in roughly 7 orders of magnitude less background than that of an electron (one order of magnitude less than a proton) [24]. The bremsstrahlung background coming from alpha-induced X-rays, as is the case with the APXS method, is significantly weaker than electron-induced X-rays generated by an X-ray tube. This complicates low-Z quantification with X-ray tube instruments in addition to the weak sensitivity to low-Z elements given the lack of PIXE to complement XRF.

1.3.2.4 Detector-Induced Satellite Peaks

Background peaks can arise from interactions within the detector and its components that, if not corrected, can result in errors in spectral assessments. If during an ionization event an excited silicon atom in the active layer fluoresces rather than emitting an Auger electron, there is a chance that photon can be lost from the active layer. In such an instance, the accumulated charge will be comparable to the incident energy of the excitation less the binding energy of silicon (1.74 keV). This gives rise to satellite peaks consistently lower
than their parent line and of equivalent FWHM. Typical amplitudes are 1-2% of the parent peak. Due to their relative low intensity, escape peaks are most often fit using a simple Gaussian. Escape peak height increases with atomic number [25]. Escape peaks can also overlap characteristic lines, as is the case with the iron escape peak and the titanium Kα line.

Pile-up peaks occur when two events occur within a short time frame such that the energy perceived by the signal processor is the sum of the two energies. Pile-up peaks can be removed during pulse processing at the expense of increased dead time. As count rate increases with respect to processing time, pile-ups are more frequent. On MER, a typical processing time is 300 μs with count rates of 60 to 70 counts per second achieved [4]. Pile-up peak amplitudes are dependent on the count rate of peaks, not the entire spectrum. A pile-up peak of even the most prominent peak, would have a peak area of only 0.2% of the parent in this the most extreme case.

1.3.3 Silicon Drift Detectors

Silicon drift detectors are charge delivery detectors. Packets of charge are drawn to a conduction channel along the centre of the wafer, and eventually the transistor, by a transverse drift field. A concentric ring structure on a SDD produces a radial drift field. Multiple ionization packets of charge can exist in the channel at once without convolution. An electric field is created due to a voltage difference between the high voltage (HV, the electric potential at the outer ring) and the back voltage (BV, the potential at the back plate) producing the conduction channel. The field that creates the channel is strong enough to prevent diffusion out of the channel [25].

SDDs have a low capacitance per area, shorter processing times that provide high throughput ability, and low volume, resulting in low leakage current and noise. SDDs also have the ability to operate at warmer temperatures through Peltier cooling. Despite comparable performance to SiLi detectors, SDDs have a limited active area and limited thickness reducing their efficiency above ∼10 keV. Due to the limited thickness, the back contact can provide spectral contamination. SDDs provide a superior peak:background ratio and tailing compared to SiLi detectors but are inferior at low energy when run with the same processing
time. ICC in SDDs is typically at the cathode contacts [25].

1.4 Considerations for Operating an X-ray Spectrometer on Mars

This section will focus on certain nuances when operating an X-ray spectrometer, like the APXS, on the surface of Mars. Specifics to how the MER APXS is tactically operated are discussed in great detail in §3. Specifics on how the MSL APXS is tactically operated, as relevant to the work herein, will be presented along with general comments.

1.4.1 In Situ Sampling and Dust

Sample preparation on Mars is very limited. Common practise in terrestrial laboratories is to homogenize (powder) a geological sample to a smooth and flat finish. On Mars, the operations team is restricted to the spacecraft’s capabilities, limiting available sample preparation options. Power or other tactical limitations may preclude possible sample preparation options within a given plan. Targets are not always flat, can be covered in a coating (such as dust), and can have heterogeneities within the instrument’s FOV, further complicating assessment even when sample preparation is possible [4, 5, 22, 29, 30].

1.4.1.1 Heterogeneities

Both MER and MSL are equipped with wire brushes to remove most of a layer of thin dust that is rather ubiquitous on the surface of Mars [3, 31, 32]. A thorough discussion of Martian dust is given by [29, 30]. There are mechanisms to account for the spectral influence of dust on measured targets (see §4.1), however, the composition and thickness of dust must be assumed to have even the slightest confidence in the modelled composition of a dust-free rock. In reality, the thickness is not well known and certainly not uniform. Whenever possible, targets are brushed by the RAT (Rock Abrasion Tool) on MER or DRT (Dust Removal Tool) on MSL. Brushing is typically only an option on flat, smooth, targets. On Mars, many targets of scientific interest are not flat, or are simply not stable enough. This can preclude the ability to place instruments close to the target and also can prohibit
grinding with the RAT on MER and using the DRT or drilling to look at sub-surface chemical changes on MSL.

Chemical heterogeneities exists across a range of scales on Mars. Measurements conducted with the APXS are, except in extremely rare situations, never pure mineral assemblages. Most relevant to the APXS are heterogeneities on the sub-cm scale through cm scale [21, 22]. These heterogeneities are most commonly veins, nodules, or other visually and chemically distinct features of diagenetic origin. In a laboratory, each of these end-members could be isolated and individually prepared for analysis. On Mars, measurements are conducted that are a convolution of the various endmembers. Analytical techniques for deconvolving the chemistry of individual endmembers is at the centre of the work presented here. The reader is encouraged to read §2.1 for a detailed presentation of the method and §2.2 for a discussion specific to targets of significant vertical relief.

### 1.4.1.2 Targeting

The APXS is deployed using a robotic arm (see Figure 2.14). The arm (Instrument Deployment Device, IDD, on MER, RA on MSL) is prone to placement uncertainty due to the ability to target using rover stereo imagery and actuator joint positioning as well as the thermal expansion and contraction of the arm [33]. Due to the greater size and mass of the MSL robotic arm (2.1 m in length, 30 kg) compared to that of MER (0.9 m in length, <5 kg), the targeting accuracy for instruments on MER is greater than on MSL. The precision is also better constrained on MER than MSL.

Targeting is incredibly important for the APXS as it is one of the few instruments on the rovers that does not always observe its own footprint and thus know precisely where was targeted. On MER, due to the higher targeting accuracy and precision, images taken with an IDD-mounted camera, the Microscopic Imager (MI), can be done as “MI finder frames”. MI finder frames are images captured where the APXS FOV centre can be approximated with great confidence. On MSL, the accuracy and precision are of the same scale as the APXS FOV, discussed further in §2.1. While it is not possible to know with the level of certainty on MER where a single MSL APXS FOV is centred, commanding multiple APXS measurements accompanied by images from the arm-mounted camera, MAHLI, provides the framework to
localize APXS measurements with much greater confidence when chemical heterogeneities exist and are tied to visual heterogeneities in the MAHLI image(s). This is discussed in more detail in §2.

1.4.2 Temperature

As discussed in §1.3, temperature contributes directly to degrading spectrum resolution. Mars, like Earth, has diurnal and seasonal temperature oscillations. In a laboratory on Earth, the temperature of the detector can be directly controlled, facilitating consistent and good resolution from spectrum to spectrum. On Mars, while tactically planned for the colder part of the Martian days, the temperature during an APXS integration can still change by more than 40°C. The firmware of the APXS on MER and MSL compensates for the drift in spectral energy scale caused by temperature. However, temperature compensation is incorrect in the MER alpha and background acquisition modes further broadening the peaks [12].

On MER, commanded APXS start and stop commands are limited in their timing for reasons discussed in §3. Thus, warmer-temperature spectra are often acquired as part of an integration but are discarded when forming a spectral sum from the (up to) 12 individual measurements. On MSL, this practise is also utilized, however, an operational Peltier cooler reduces the temperature of the APXS detector and is automatically activated at temperatures above -50°C, improving spectral resolution during the warmer mornings and afternoons on Mars. The use of a Peltier cooler on MSL provides good resolution APXS spectra during temperatures on Mars that are warm enough to operate the RA without the added power demand of arm heating. The increased operational temperature range facilitates touch-and-gos and “rasters”, central to the deconvolution and localization method (§2). Daily average temperatures at Gale Crater range from 210 to 230 K with a 50 to 70 K range over a given sol and a seasonal range of 190 to over 270 K. APXS measurements typically avoid the warmer parts of a Martian day, integrating primarily during temperatures in the 190-240 K range. A full report on temperatures recorded by MSL is given in [34].
1.4.3 Atmosphere

On Earth, samples are often measured using XRF or PIXE in vacuum. On Mars, the APXS is engulfed by an atmosphere that changes in density (pressure) and relative composition on daily and seasonal timescales. Seasonal average daily pressure within Gale Crater, as measured by MSL, varies from approximately 750 to 900 Pa over the course of a Mars year, and by 60 to 100 Pa over the course of a single sol [34]. The atmosphere preferentially attenuates low-energy X-rays producing a sample-instrument separation dependance on peak area especially for the low-energy peaks like sodium. Furthermore, while the bulk of the constituents of the atmosphere of Mars are “invisible” to the APXS, argon, at approximately 2% v/v [13], is measured by the APXS contributing a background in the 3 keV region in all spectra.

Measurements with the MER APXS have specifically targeted the atmosphere, observing variability in atmospheric argon density. These measurements represent the only high-frequency long-duration measurements of argon in the atmosphere of Mars from the surface. Due to the number and duration of measurements obtained, a summed spectrum sheds light on the background of the MER APXS instrument and its changing environment over the course of its mission since landing in 2004. A thorough discussion of atmospheric measurements with the MER APXS is presented in §3.

1.4.4 Latency

The physical distance separating Earth and Mars results in the inability to operate spacecraft and observe experiments in real time. Commands are sent to MER and MSL, direct from Earth, using radio waves, arriving 4 to 21 minutes after initial transmission. Data are obtained from the rovers primarily via orbiter relay. §3 discusses in greater detail the nuances of dealing with latency and the differences between a work day on Earth and the rover’s work day on Mars. The timing of rover operations is further complicated given the landing sites of MSL and MER-A are on opposite sides of the planet from MER-B [6, 31].

The separation between Earth and Mars means all commands must be pre-planned and executed by the rover on its own. Data downlink comes later, depending on the timing
and availability of orbiter passes. In many instances, there are opportunities to conduct science but the necessary data for targeting or the status of the spacecraft are not received until after the Earth work day, further slowing the ability to conduct science. Any technical issues can only be fixed remotely - it is impossible to perform physical repairs to damaged equipment. These issues do not exist within Earth laboratories.

1.4.5 APXS Spectral Backgrounds on Mars

Gamma rays (gammas, $\gamma$) arise as a result of nuclear transitions and freely exist in space. Gammas are generated in the atmosphere of planets, like Mars, due to interactions between cosmic rays and particles in the atmosphere. As a result, a certain level of gamma radiation will exist naturally on the surface of Mars. In the special case of MER, the Mössbauer (MB) spectrometer generates gammas during the natural decay of its sources [35]. While mitigated through tantalum shielding, a clear gamma-induced background is observed that decays at the same rate as the MB sources. This is discussed in more detail in §3 and manifests in a slowly varying linear background due to partial energy deposition of the $\gamma$-rays during interaction with the X-ray SDD. The $^{244}\text{Cm}$ sources are also a source of (42.8 keV) $\gamma$-rays.

1.4.6 MSL APXS Operations

Operation of the MSL APXS instrument is subject to many of the same considerations as the MER instrument. Differences arise due to the different performance of the MER and MSL spacecraft and also the MER and MSL APXS instruments. A thorough description of MSL operations is provided by [31].

When APXS targets are selected, flat, homogenous, dust-free are preferred for cold, long-duration measurements in close proximity to the sample. Close proximity to the sample improves counting statistics and reduces errors as the flux of detected photons trends as $\sim r^{-2}$, in theory. A geometric normalization factor (norm) is used as a proxy for instrument standoff and is calculated using the relative peak areas in a spectrum. It has been observed that norm drops off with standoff to approximately the 2nd power. The deviance from $r^{-2}$ is likely due to the APXS FOV growing slower with increasing standoff than the flux drops off. Standoff is defined as the separation between the APXS instrument face and the sample
surface. To a good approximation, the count rate of a spectrum is halved with every cm increase in standoff [22].

1.4.7 Composition Determination

To quantify constituents in a sample, an acquired spectrum is first fit to obtain peak areas for the various elements (or oxides) within a sample. §4.2.2 discusses spectrum fitting (for the purposes of spectral simulations) in greater detail. Relative line intensities for each element are locked with a few exceptions.

Signals not sourced from the sample need to be considered. The overlap of the Zr L-line sourced from the detector collimator with phosphorus Kα peak causes an extra background further exacerbated by phosphorus’s proximity to the spectrum-dominating silicon peak. Additionally, potassium overlaps the scattered Pu M-lines while the scattered X-rays from the titanium foils increases uncertainty in the derived titanium concentration.

Once peak areas are tabulated, a standard matrix is presumed. Yields are obtained and iteratively compared to the observed, taking into account the impact of matrix effects discussed in §1.2.3.4. Normalizing the oxides to 100% is common practise, removing the need to determine absolute efficiency. A detailed discussion of composition determination with the APXS can be found in [4, 5].

1.5 Introduction to Published and Submitted Manuscripts

This section will serve as an introduction specific to each of the three manuscripts presented within the body of this thesis in addition to provide the motivation behind each paper. The formatting of each manuscript has been modified to match this thesis but the content, including the use of American English, has been unaltered.
1.5.1 Deconvolution of distinct lithology chemistry through oversampling with the Mars Science Laboratory Alpha Particle X-Ray Spectrometer

The published work presented in §2.1 is on an analytical method deconvolving the chemistry of visual endmembers within APXS data, achieving analytical values and errors for the first time. Prior to the development of the method, the APXS team would estimate enrichments through chemical gradients.

The work was initially motivated through the incorrect interpretation of APXS data from the Sayunei target (illustrated in Figure 2.3). The APXS FOVs were initially assumed to be positioned in such a way that they were mostly absent vein material. The interpretation as a result was that the host bedrock was enriched in sulphur. An early iteration of the present-day program was written to show an ideal correlation between \( \text{SO}_3 \) measured and abundance of vein material in the APXS FOV (weighted by radial sensitivity) is achievable within arm placement uncertainty (see §1.4.1.2). This showed conclusively that the host bedrock was not enriched in sulphur. The analysis program matured prior to publication to be able to handle more than two endmembers by solving a non-invertible, non-negative, bounded, matrix equation through least-squares minimization.

The paper focuses specifically on the deconvolution method. However, the results presented are important to note. The first target, Sayunei, demonstrates stoichiometric Ca:S consistent with pure calcium sulfate. Deviation from the ideal Ca:S ratio is explained by preferential attenuation of Ca within CaSO\(_4\). The result contributed to an earlier publication in Science [36]. The target Stephen (Figure 2.7) is of significant scientific speculation due to its high-Mn content. The work published provides the only dust-free APXS values of the target. These values are used in layer modelling discussed later (§4.1). Lastly, study of the APXS target Morrison (Figure 2.9) shows the bedrock endmember in close compositional agreement with a nearby bedrock measurement. The feature chemistry, when deconvolved from the bedrock chemistry, shows significant enrichment in magnesium, nickel, and sulphur, consistent with 11\% of 40:30:3 molar Mg:S:Ni magnesium-, nickel-sulfate addition to the local bedrock. In parallel with work conducted in §2.2, this provides strong evidence of
either multiple fluid events or an evolving fluid impacting the chemistry within ancient Gale Crater.

1.5.2 Modeling and mitigation of sample relief effects applied to chemistry measurements by the Mars Science Laboratory Alpha Particle X-ray Spectrometer

The published work presented in §2.2 builds on the work presented in §2.1, focusing on the (potential) effects of target relief on APXS analyzes and offers operation guidance as to when target relief is a concern and discusses for the first time a technique how to mitigate target relief with little tax on operational limits and complexity.

The APXS vertical sensitivity has been documented previously for MER in [5] and is a similar response curve to that of MSL. Simulations were conducted to investigate the scenario of a cylinder of unique chemistry within the APXS FOV. Various heights, diameters, and positions within the FOV were tested using the vertical and radial sensitivity of the APXS (see §4.2.1) to better understand instrument behaviour (Figure 2.15 and Figure 2.16).

The paper focuses specifically on simulations and the method, discussing specifically results from three targets on Mars. Morrison is investigated once again, considering target relief for the first time and comparing the result to previously published values that assumed a flat target (§2.1). Due to the small scale in relief (~4 mm) and the slowly varying change, the 3D result was within experimental uncertainty of the previously published 2D result. This also provides a consistency check for the 2D and 3D method. A light-and-dark vein network Alvord Mountain (Figure 2.18) also demonstrated agreement between the models investigated. Specifically, three models were conducted (flat, 3D, and 3D with APXS docked normal to the surface) and showed that despite the 10+ mm change in vertical relief, due to the small changes on the scale of the APXS FOV, the models were in agreement. Lastly, a cylinder-like nodule Sperrgebiet (Figure 2.19) was analyzed both considering and neglecting target relief. Due to the sharp and large-scale contrast in relief (9 mm), the 3D and 2D models did not agree, emphasizing the importance of considering target relief in this case. Furthermore, the chemistry of the nodule is consistent with 15% magnesium sulfate addition
to the local bedrock. In parallel with work conducted in §2.1, this provides strong evidence of either multiple fluid events or an evolving fluid impacting the chemistry within ancient Gale Crater.

1.5.3 Seasonal atmospheric argon variability measured in the equatorial region of Mars by the Mars Exploration Rover Alpha Particle X-ray Spectrometers: Evidence for an annual argon-enriched front

The submitted work presented in §3 represents the most-through study of APXS atmospheric data ever conducted. The manuscript provides a thorough description of MER APXS operations with specific considerations for the instrument on a decade-old rover. A detailed discussion of the atmospheric data follows, probing instrument behaviour and response in a much easier fashion than with traditional geologic samples. Various models are tested on high-frequency MER-A atmospheric measurements taken over the course of a couple weeks. Absent a calibration of gaseous samples, this work presents a first proof of concept that the data and analysis method can be relied on. The best model is applied to the many years of MER-B APXS atmospheric data. The MER-A results are consistent with the ideal gas law.

The MER-B atmospheric data shows agreement with past surface pressure-monitoring spacecraft in terms of timing and relative variation. There is an observed spike in argon density during southern spring. Orbiters and other surface spacecrafts have not attempted to or are unable to observe this brief argon density surge we interpret as a wave of argon fleeing the polar cap region. The observation could provide significant implications for atmospheric and climate modelling. Furthermore, given the 1,600+ hours of good-temperature atmospheric data, incredible statistics can be achieved by a carefully summed spectrum. Upon doing so, several background features, from the APXS instrument and its surrounding environment, are visible and quantifiable for the first time, as is a background feature of unknown origin.
Chapter 2

Published Articles

Included in this chapter are two published manuscripts. The appropriate copyright can be found at the end of each abstract. Formatting as well as figure, table, and reference numbers have been changed to be consistent throughout this thesis. Figures and table locations within deviate from the published manuscript.

2.1 Deconvolution of distinct lithology chemistry through oversampling with the Mars Science Laboratory Alpha Particle X-Ray Spectrometer


2.1.1 Abstract

The Alpha Particle X-Ray Spectrometer (APXS) determines the chemical composition of Martian rocks and soils on-board both active National Aeronautics and Space Administration (NASA) rovers using X-ray emission spectroscopy through complementary particle-induced X-ray emission (PIXE) and X-ray fluorescence (XRF) excitation methods. A single APXS spectrum represents the sum of the signals from within the instrument’s field of view (FOV). In the past, features smaller than the FOV have been investigated through repeated
measurements with stepwise lateral offsets. These lateral offsets allow for empirically extracting, through elemental correlations, distinct compositions of different features. Here, we present a novel analytical method for deconvolving the endmember chemistry of visually distinct components through oversampling and the integrated analysis of the elemental data and supporting images. We discuss specifically the method’s application to three targets investigated by the Mars Science Laboratory rover Curiosity during its traverse, as well as the added information that can be gained from this method in the future. © 2016 John Wiley & Sons, Ltd.

2.1.2 Introduction

The Mars Science Laboratory (MSL) rover Alpha Particle X-Ray Spectrometer (APXS) is a robotic arm-mounted chemical analysis instrument that performs high-precision in situ measurements of rocks and soils [5]. The APXS detects and quantifies the concentrations of elements from Na to Y and beyond in a field of view (FOV) approximately 1.5 cm in diameter. Gellert et al. [5] provide further background on the APXS instrument and its method. The MSL APXS is roughly five times more sensitive than its Mars Exploration Rover (MER) predecessor and is equipped with a Peltier cooler improving the nominal ambient operational temperature from 40°C to 5°C[10]. The increased instrument sensitivity and improved resolution during periods of warmer temperatures results in the MSL APXS being more amenable to raster investigations than the earlier MER instruments.

In accord with NASA terminology (MER and MSL), an APXS integration is used to describe the sum of data stored in an APXS spectrum over a specified duration. The majority of spectra are taken in a sensor-defined so-called “contact geometry” or at sample-instrument distances only slightly greater. This yields excellent statistics for major, minor, and trace elements after 4 hours of integration. However, a 10- to 20-minute integration provides acceptable statistics even for most trace elements.

Alpha Particle X-Ray Spectrometer “rasters” involve laterally offset spots from a primary target and are regularly accomplished on MSL with 20-minute APXS integrations followed by a several-hour overnight integration on the primary target. This approach assesses the homogeneity of the target and can provide an estimate for varying dust coverage with as
few as two spots. For specific small targets - such as a vein or diagenetic feature - a raster typically comprises four measurements with the successive FOVs centered at the corners of a square in addition to the centrally placed overnight integration. On MSL, the offset spots can be investigated in the morning or evening during temperature windows favorable for spectrum resolution without the need for rover arm actuator heating.

The Mars Hand Lens Imager (MAHLI) is a camera that, like the APXS, is mounted on the turret at the end of the arm on the MSL rover, Curiosity. The 2-megapixel Bayer pattern color charge-coupled device (CCD) camera is complete with a macro lens and provides images from the Martian surface with sufficient resolution to discern individual grains as small as 30-40 \(\mu\)m in size [37]. In addition to conducting stand-alone science campaigns, MAHLI routinely documents APXS targets with a 5-cm hover, providing a similar scale to MER APXS documentation images [38]. These MAHLI images are essential for the interpretation of APXS spectra and have a spatial resolution of about 31 \(\mu\)m per pixel.

Alpha Particle X-Ray Spectrometer rasters were originally implemented as a means to guard against uncertainty in rover arm placement. APXS and MAHLI are located on opposite sides of a 60-cm diameter, 30-kg turret at the end of the 2.1-m long arm. Deploying either instrument based on the acquired navigation or hazard camera stereo imagery [39] is prone to a placement uncertainty (accuracy) of up to 20 mm [33]. Moreover, the tool change from MAHLI to APXS (or vice versa) can result in a spatial misalignment between the MAHLI documentation image centers and the center of the APXS FOV of up to 15 mm in any direction. Additionally, the uncertainty in precision absent tool change is at most 10 mm. MAHLI documentation of visible surface contact by turret-mounted tools like the APXS, dust removal tool, and drill averages 3 mm for a set of 18 different targets with observable surface contact. Nominally, the APXS does not disturb the target even when deployed to contact; however, when deployed to soils or drill fines, the contact sensor can visibly compress the unconsolidated material before triggering contact and stopping rover arm motion. In these 18 cases of visible contact by turret-based tools, the observable offsets varied from around 0.5 to 5.0 mm. The tool center was shifted predominantly towards the right in the default MAHLI image orientation with respect to the center of the MAHLI 5-cm standoff images.
Placing the target of interest in the center of a $2 \times 2$ APXS raster with 2 cm side lengths guarantees that a small-scale feature is captured sufficiently in at least one APXS spectrum. Through overlaying MAHLI images and assessing the weighted contribution of orthogonal and visually distinct components within the APXS FOV, the bulk chemistry of each component distinguishable in the MAHLI images is determined in an iterative process that treats the exact position of each APXS spot as a parameter that is varied and optimized. Analyses of the Martian targets Sayunei, Stephen, and Morrison encountered by the Curiosity rover are presented here and summarized in Table 2.1.

### 2.1.3 Method

A single APXS spectrum represents the weighted sum of the signals from within the instrument’s FOV. The emission of alpha particles and Pu L X-rays from the six $^{244}$Cm sources in addition to detector collimation produces a radially dependent spectral sensitivity where a small surface area contributes more to the spectrum near the center of the FOV than at the extremities. This sensitivity has been investigated and determined through both laboratory testing and Monte Carlo simulations. Variations in target relief also contribute to spectrum sensitivity. The APXS FOV diameter is dependent on the distance between the instrument sensor head and sample, increasing with standoff distance. The apparent standoff, and thus FOV size, is empirically determined from the spectrum geometric normalization factor (norm), which was calibrated through laboratory testing and experiments performed on Mars using the MER APXS [5].

Each pixel in a MAHLI image is classified orthogonally. That is, each pixel is optically distinguishable and contributes to a single phase only. We use the term phase to define a visually distinct component of a MAHLI image, e.g. dusty part of a rock, a vein feature or the dust-free portion of bedrock. Using the norm as a proxy for standoff, the APXS FOVs corresponding to the standoff and acceptance angle are superimposed onto the image. The high precision of rover arm placement supports the relative positions of APXS FOVs within a raster to be locked throughout the routine. The initial center of a raster assumes alignment with the center of the MAHLI image; the subsequent iterations translate the raster laterally and/or rotate it about the raster center.
Pixels are tabulated by radial weight (and sample relief, if applicable) for each phase classification within each FOV in the raster; the radial sensitivity of the instrument results in 50% of the spectrum coming from the innermost 16% of the FOV area as shown in Fig. 2.1. The raster is then translated and/or rotated about the raster center with the pixel-based phase abundances re-calculated for each new orientation. The phase coverage error is the larger of a relative percentage of the phase abundance value and a defined absolute minimum. The relative percentage and absolute minimum are defined based on the optical contrast between orthogonal phases. For all positions, the weighted contribution of each phase is compared with the acquired APXS spectra. For two-phase systems, the raster is localized by minimizing the chi-square of the linear relationship between the abundance of an observed phase of distinct chemistry for each APXS spot and the chemistry of each spot measured by the APXS [40] as conceptualized in Fig. 2.2. The linear correlation between phase abundance and measured APXS chemistry is fit using a bivariate weighted linear regression [41]. For complex targets of multiple phases, the raster is localized by finding the raster position that minimizes

\[(C \cdot x - d)^2\]  

where \(C\) is a matrix corresponding to the abundance of each phase in each FOV, \(x\) is a matrix corresponding to the chemistry of each phase, and \(d\) is the APXS-measured chemistry for each FOV. Bounds are applied to ensure proper normalization and non-negativity. The minimization directly solves for \(x\), providing the endmember phase chemistry. Note that matrix attenuation differs in bedrock compared with pure calcium sulfate. Concentrations derived by Gellert et al. [5] (reported in R. Gellert [40]) assume a homogeneous matrix, reducing accuracy of the measured concentrations, \(d\), in heterogeneous targets including features such as veins.

To deconvolve the composition of visually distinct phases of targets in Table 2.1, the algorithm assumes the following:

- visually distinct phases have a distinct chemistry that is homogeneous on the scale of the feature;
each visually distinct phase is infinitely thick compared with the APXS sampling depth (on the order of less than a mm - with 90% of X-rays generated in the top 5 \( \mu \)m for Si, 10 \( \mu \)m for Ca, and 75 \( \mu \)m for Fe - further described in Gellert et al., [5] Rieder et al., [4] and Campbell et al. [11]);

- the APXS and MAHLI are placed normal to the sample surface;
- the target is flat;
- the relative placement uncertainty of FOVs within the raster is negligible (i.e. the error is in the overall raster placement accuracy not relative placement of the FOVs); and
- the contribution of a relative position within a FOV (r/R) is independent of FOV size.

### 2.1.4 Results

Rocks at the MSL landing site, Gale Crater, Mars, are primarily of sedimentary origin, composed of clasts, grains of various sizes, and mineral precipitates that vary in composition, leading to chemical heterogeneity on the centimeter scale and smaller [42]. Understanding the composition of the different components of these sedimentary rocks is key to interpreting ancient Martian geologic processes. The first MSL APXS raster investigated a target named Sayunei displayed in Fig. 2.3. The Sayunei target was a mudstone of the Sheepbed member - part of the Yellowknife Bay formation [43] - with a well-defined, light-toned cross-cutting vein [36]. The light/dark contrast between the vein and host mudstone in the MAHLI color image provided the visual distinction required to orthogonally classify pixels as either vein or dusty rock as captured in Fig. 2.4. The APXS data collected from a \( 2 \times 2 + 1 \) raster, illustrated in Fig. 2.5, showed elevated CaO and SO\(_3\) concentrations in three of the five raster positions as shown Fig. 2.6. This light-toned vein material is interpreted to be CaSO\(_4\) [36] based on the stoichiometrically correct correlation of CaO and SO\(_3\) in the five APXS spectra. As illustrated in Fig. 2.2, as the amount of vein material in the APXS FOV increases, the CaO and SO\(_3\) measured by the APXS will increase. This linear correlation between vein material and SO\(_3\) concentration was used to infer an APXS raster position.
that not only agrees with linear proportionality but also with the endmembers of dusty rock and CaSO\(_4\). A raster position for Sayunei exists within arm placement uncertainty such that the elevated CaO and SO\(_3\) concentrations observed are attributed to the vein material as opposed to being elevated in the host rock as illustrated in Figs. 2.5 and 2.6. Chemistry data for the dusty bedrock and vein are presented in Table 2.2.

Figure 2.7 captures Stephen, a small rock with a thin, dark-toned surface fracture fill at the Kimberley waypoint that was partially cleared of dust by a mast-mounted laser ablation instrument, ChemCam [44]. APXS data collected from a \(2\times2 + 1\) raster showed variation in the APXS norm as well as concentrations of elements associated with Martian dust. The APXS raster was complemented by 5-cm standoff MAHLI images on all APXS raster spots, constraining the rotation and relative positions of the APXS FOVs. Figure 2.8 compares the MAHLI image RGB and HSV coloring of Stephen facilitating a more direct pixel classification as either dust or bare rock based on pixel saturation level. Pixels were also classified as negligible based on surface relief as the bedrock was several centimeters below the target rock. This combination of elemental-based and relief-based linear relationships inferred a more representative APXS raster position of the manganese-rich target and provided an estimate of the dust-free composition. Additionally, pixel saturation in Fig. 2.8(b) appears to capture variability in dust thickness. Endmember chemistry data for both the dusty rock and bare rock are presented in Table 2.3.

Figure 2.9 displays Morrison, a brushed, raised, and resistant nodular feature at the Pahrump waypoint interpreted as diagenetic [45]. APXS data obtained via a \(2\times2 + 1\) raster showed elevated MgO, SO\(_3\), and Ni concentrations in the diagenetic feature relative to the immediately adjacent bedrock. MAHLI images of the target were acquired on earlier sols of the central APXS raster spot only. As with Stephen, a ternary pixel classification system was employed binning pixels orthogonally as dust, bare rock, or diagenetic feature as illustrated in Fig. 2.10. The goal was to localize the APXS raster through improved elemental correlations and determine the bulk chemistry of the host rock and diagenetic feature, presented in Table 2.4. The bulk chemistry of the host rock closely matched that of a nearby brushed bedrock target named Maturango. Figure 2.11 illustrates the improved correlation between measured Ni concentration and diagenetic feature FOV coverage after
raster localization, as illustrated in Fig. 2.12. The composition of the Morrison feature is consistent with the feature comprising a mixture of substrate bedrock chemistry and an added component supporting the interpretation of Morrison and other raised, resistant features at this location as diagenetic in origin. This added component is inferred through the addition of an unknown bulk chemistry to the bare bedrock. Assuming the minimum elemental concentration ratio of diagenetic endmember to bare rock endmember, we estimate that the diagenetic feature is composed of approximately 89% host rock and 11% of an added component. This assumes that the added component is absent SiO$_2$ and all SiO$_2$ in the diagenetic feature arises from the host rock. Under this assumption, the added component has a stoichiometric Mg:S:Ni molar ratio of roughly 40:30:3. This is consistent with the addition of a Mg-, Ni-sulfate-rich mineral to the bedrock producing the diagenetic feature. The chemistry of the added component is presented in Table 2.4.

As shown in Figs. 2.5 and 2.11, improved knowledge of the position of APXS rasters through MAHLI pixel analysis resulted in 4-8 mm offsets between the APXS raster center and the center of the MAHLI image – a significant offset considering the size and sensitivity of the APXS FOV. The raster offset was smaller from the center of the 5-cm standoff images than the 25-cm standoff image as expected. APXS placement deviation from the center of MAHLI images is comparable with observed offsets between the imprint of turret-mounted tools and the documenting MAHLI image center. APXS raster edges are not parallel to MAHLI image edges, as confirmed when MAHLI images are acquired on each APXS raster spot. Rotation deviation from the original suite of MAHLI 5-cm standoff images on Stephen was minimal, further supporting the high precision of rover arm movements. The best agreement raster offsets from MAHLI image center for all three raster analyses are in a similar direction with respect to the default MAHLI image orientation, despite varying arm orientation and rover direction. The offsets are also directionally in agreement with the 18 observable offsets between MAHLI 5-cm image centers and surface contact by turret-mounted tools.

Having variable areal abundances for each phase reduces phase composition errors. The ability to deconvolve the chemistry of distinct features depends on the feature size and position within a FOV as well as the corresponding element or oxide limit of detection.
APXS placement error on MSL results in raster localization uncertainty and thus an increase in phase contribution uncertainty, restricting the use of the algorithm to typically four or more spots. If placement uncertainty was negligible on the scale of the MSL APXS radial sensitivity, the technique could be applied to single-spot APXS measurements and thus compensate for phases of known composition such as the global Mars dust [29]. On MER, Microscopic Imager (MI) finder frames assist in localizing the center of the APXS FOV. However, MI finder frames are monochromatic, necessitating the overlay of colored Pancam images for most analyses. Furthermore, MER APXS rasters are rare, limiting the technique beyond single-spot dust compensation.

2.1.5 Discussion and conclusions

The development of the model and algorithm described herein has expanded the capability of the APXS. The technique will be applied to the MER APXS dataset to provide dust-free composition of targets where possible and phase-specific chemistry of targets where rasters were acquired. As the Curiosity rover continues to utilize APXS rasters, the offset between the MAHLI image center and APXS raster center will be investigated to determine if a MI-finder-frame equivalent can be incorporated. The preliminary analysis of another MSL APXS raster, analyzing black and white erosion-resistant veins at the Garden City outcrop, further supports the common offset direction from MAHLI image center. MAHLI focus merge data products provide a relative surface relief map of a target using the camera’s focusing mechanism and can assist in compensating for the impact of irregular target relief. This analysis, along with varying how the APXS was deployed during a raster, is under development and will allow pixel weighting to model APXS deployment angle, target relief, and instrument radial sensitivity. Additionally, the orthogonal binning of pixels can be automated and complemented with a user-friendly interface. The minimization technique in Eqn 2.1 has proven useful in investigations of the many-phase Martian targets Pinnacle_Island and Stuart_Island encountered by the Opportunity rover, as utilized in Arvidson et al. [In Press] This least-squares minimization will be applied to future rasters not only on Mars but also in the laboratory to investigate heterogeneous samples including, for example, the recently discovered NWA 8171 Martian meteorite.
The complementary use of PIXE and XRF on the APXS provides excellent sensitivity and precision for determining major, minor, and trace elements of increasing mass from Na in rocks and soils on Mars. On MSL, through rastering, visually heterogeneous Martian targets can be thoroughly characterized with five separate interrogation spots on a single Mars day. With the support of MAHLI images, APXS rasters of optically distinct features can be localized and provide chemistry on a scale smaller than the APXS FOV. Analytical APXS chemistry on millimeter-scale targets of interest is achieved for the first time both on Earth and on Mars with important implications for elucidating the formation mechanisms of various rocks on Mars.

2.1.6 Acknowledgments

This work has been supported by the Canadian Space Agency (CSA) under contract 9 F052-14-0592. The MSL APXS is financed and managed by the CSA. MacDonald Dettwiler and Associates was the primary contractor to build the instrument. Funding for the APXS science team is provided by the CSA and NASA. Much appreciation goes to NASA/JPL for their support, dedication, and invaluable expertise during development and operations.

2.1.7 Tables

Table 2.1: Overview of APXS raster targets. Sol corresponds to the number of elapsed Martian days since landing. Due to the night-time ultraviolet imaging campaign on the target Sayunei, a single 25-cm standoff Mars Hand Lens Imager (MAHLI) context image was used for the analysis instead of the typical higher-resolution 5-cm standoff documentation image. MAHLI documentation images on Stephen were acquired on each Alpha Particle X-Ray Spectrometer (APXS) spot constraining raster rotation.

<table>
<thead>
<tr>
<th>Target Name</th>
<th>Sol</th>
<th>Raster</th>
<th>MAHLI Images Utilized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sayunei</td>
<td>165</td>
<td>2×2 + central overnight spot</td>
<td>Single 25-cm standoff context image</td>
</tr>
<tr>
<td>Stephen</td>
<td>627-629</td>
<td>2×2 + central overnight spot</td>
<td>5-cm standoff APXS documentation image for each APXS spot</td>
</tr>
<tr>
<td>Morrison</td>
<td>767-779</td>
<td>2×2 + central overnight spot</td>
<td>Single 5-cm standoff APXS documentation image</td>
</tr>
</tbody>
</table>
Table 2.2: Endmember concentrations of the vein target Sayunei obtained through least-squares minimization. Errors correspond to the range of each element that increases the $\chi^2$ by 1. Correlation coefficients, R, are included.

<table>
<thead>
<tr>
<th></th>
<th>Dusty Rock</th>
<th>Vein</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc.</td>
<td>Error</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>2.75</td>
<td>0.10</td>
</tr>
<tr>
<td>MgO</td>
<td>9.58</td>
<td>0.12</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.65</td>
<td>0.12</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>43.08</td>
<td>0.18</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>1.01</td>
<td>0.04</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>5.38</td>
<td>0.11</td>
</tr>
<tr>
<td>Cl</td>
<td>1.54</td>
<td>0.02</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.55</td>
<td>0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>5.54</td>
<td>0.07</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.90</td>
<td>0.03</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.40</td>
<td>0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>0.31</td>
<td>0.01</td>
</tr>
<tr>
<td>FeO</td>
<td>20.12</td>
<td>0.11</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>817</td>
<td>30</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>827</td>
<td>20</td>
</tr>
<tr>
<td>Br (ppm)</td>
<td>240</td>
<td>5</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2.3: Endmember concentrations of the manganese-rich Stephen target obtained through least-squares minimization. Errors correspond to the range of each element that increases the $\chi^2$ by 1. Correlation coefficients, R, are included.

<table>
<thead>
<tr>
<th></th>
<th>Dusty Rock</th>
<th>Bare Rock</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc.</td>
<td>Error</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.16</td>
<td>0.09</td>
</tr>
<tr>
<td>MgO</td>
<td>17.53</td>
<td>0.21</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4.59</td>
<td>0.1</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>34.42</td>
<td>0.2</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.73</td>
<td>0.04</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>4.71</td>
<td>0.06</td>
</tr>
<tr>
<td>Cl</td>
<td>3.29</td>
<td>0.04</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.4</td>
<td>0.05</td>
</tr>
<tr>
<td>CaO</td>
<td>4.38</td>
<td>0.05</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.9</td>
<td>0.03</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.35</td>
<td>0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>3.14</td>
<td>0.05</td>
</tr>
<tr>
<td>FeO</td>
<td>21.42</td>
<td>0.15</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>907</td>
<td>45</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>7088</td>
<td>145</td>
</tr>
<tr>
<td>Br (ppm)</td>
<td>1960</td>
<td>40</td>
</tr>
<tr>
<td>Total</td>
<td>100.02</td>
<td>99.99</td>
</tr>
</tbody>
</table>
Table 2.4: Endmember concentrations of the diagenetic feature Morrison obtained through least-squares minimization. Measured chemistry of nearby brushed bedrock target Maturango included for quick comparison with the bare host rock endmember. Added component assumes zero SiO$_2$ concentration and contributes 11% to the diagenetic feature. Errors of dusty rock, bare rock, and diagenetic feature endmembers correspond to the range of each element that increases the $\chi^2$ by 1. Errors of nearby target Maturango are those quoted in Gellert [40] corresponding to statistical errors (precision or repeatability). Correlation coefficients, R, are included.

<table>
<thead>
<tr>
<th>Element</th>
<th>Nearby Brushed Rock</th>
<th>Bare Host Rock</th>
<th>Dusty Host Rock</th>
<th>Diagenetic Feature</th>
<th>Added Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>2.92</td>
<td>0.14</td>
<td>2.65</td>
<td>0.16</td>
<td>2.38</td>
</tr>
<tr>
<td>MgO</td>
<td>4.5</td>
<td>0.17</td>
<td>5.53</td>
<td>0.18</td>
<td>6.41</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>10.43</td>
<td>0.29</td>
<td>10.05</td>
<td>0.24</td>
<td>9.62</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>51.88</td>
<td>0.54</td>
<td>50.02</td>
<td>0.33</td>
<td>49.38</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>31.88</td>
<td>0.54</td>
<td>30.02</td>
<td>0.33</td>
<td>29.38</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>5.17</td>
<td>0.08</td>
<td>6.44</td>
<td>0.19</td>
<td>6.98</td>
</tr>
<tr>
<td>Cl</td>
<td>0.97</td>
<td>0.04</td>
<td>0.97</td>
<td>0.04</td>
<td>0.97</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.57</td>
<td>0.04</td>
<td>0.57</td>
<td>0.04</td>
<td>0.57</td>
</tr>
<tr>
<td>CaO</td>
<td>3.77</td>
<td>0.04</td>
<td>4.01</td>
<td>0.08</td>
<td>4.71</td>
</tr>
<tr>
<td>MgO</td>
<td>0.34</td>
<td>0.01</td>
<td>0.34</td>
<td>0.01</td>
<td>0.34</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03</td>
<td>0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>FeO</td>
<td>16.93</td>
<td>0.2</td>
<td>16.57</td>
<td>0.19</td>
<td>15.88</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>16.93</td>
<td>0.2</td>
<td>16.57</td>
<td>0.19</td>
<td>15.88</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>1732</td>
<td>55</td>
<td>1727</td>
<td>55</td>
<td>2247</td>
</tr>
<tr>
<td>Br (ppm)</td>
<td>1732</td>
<td>55</td>
<td>2277</td>
<td>70</td>
<td>2217</td>
</tr>
<tr>
<td>Total</td>
<td>99.91</td>
<td>99.99</td>
<td>100.01</td>
<td>99.99</td>
<td>100.18</td>
</tr>
</tbody>
</table>

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2.1.8 Figures

Figure 2.1: Alpha Particle X-Ray Spectrometer radial sensitivity illustrated as concentric rings centered on the Morrison target. Each ring encloses an additional 10% of the contribution to a spectrum. Fifty percent of the spectrum comes from the innermost 16% of field of view area.
Figure 2.2: Graphical representation of the relationship between increasing abundance of a visually distinct component (red part of each pie chart) within an Alpha Particle X-Ray Spectrometer (APXS) field of view (FOV) and the corresponding measured concentration: (a) illustrates an enrichment where the intercept is an estimate of the concentration of the surrounding component (bedrock) and extrapolating to 100% produces an estimate of the concentration of the primary component itself and (b) illustrates the equivalent for a depleted element or oxide within the investigated feature compared with the surrounding component.

Figure 2.3: Mars Hand Lens Imager 25-cm standoff context image of the Sayunei vein target and surrounding area.
Figure 2.4: Automated orthogonal pixel classification of the original in (a) as either vein (green) or dusty rock (unaltered) in (b).

Figure 2.5: Original Sayunei raster location (left, white, dashed) and localized Alpha Particle X-Ray Spectrometer (APXS) fields of view (FOVs) (right, yellow, solid) illustrating an 8-mm shift from the original MAHLI 25-cm context image center with raster edges parallel to image frame. Note that the image has been cropped. Additionally, exterior FOV spots were deployed to standoff, and interior FOV was deployed to contact as this was the first MSL APXS raster activity on Mars.
Figure 2.6: Comparison of the original (left) and improved (right) raster location illustrates a position within arm placement uncertainty that explains the variance in CaO and SO$_3$ (SO$_3$ shown here) arising from the varying abundance of a CaSO$_4$ vein in the Alpha Particle X-Ray Spectrometer fields of view, indicating SO$_3$ is not enriched within the host rock. Ordinate error bars that are not illustrated are smaller than the dimensions of the data points.

Figure 2.7: Mars Hand Lens Imager image of the target named Stephen. Alpha Particle X-Ray Spectrometer fields of view were placed targeting the dark-toned, dust-free portion of the rock and overhung the edge. These overhang regions were ignored due to their negligible contribution to the spectrum arising from low relief and large off-nadir distance.
Figure 2.8: Automated dust classification on Stephen. The red, green, and blue coloring is illustrated in (a) and hue, saturation, and darkness in (b). The saturation level (bright blue) is easily observed as a potential proxy for dust thickness.

Figure 2.9: Mars Hand Lens Imager 5-cm standoff Alpha Particle X-Ray Spectrometer documentation image of the diagenetic feature named Morrison.
Figure 2.10: Phase classification of the diagenetic feature Morrison. Automated pixel classification as dust, illustrated in green, and bare bedrock substrate, in red. The diagenetic feature was manually classified and is shown in blue.

Figure 2.11: Morrison phase analysis of the planned (top) and localized (bottom) raster locations. The improvement in linear response related to the diagenetic feature is evident and also pushes the feature-free endmember close to Maturango, a nearby brushed bedrock.
Figure 2.12: Morrison planned raster location (left, white, dashed) and localized Alpha Particle X-Ray Spectrometer fields of view (right, yellow, solid) illustrating a 4 mm shift from the Mars Hand Lens Imager image center.
2.2 Modeling and mitigation of sample relief effects applied to chemistry measurements by the Mars Science Laboratory 

Alpha Particle X-ray Spectrometer 


2.2.1 Abstract

The Alpha Particle X-ray Spectrometer (APXS) onboard the Mars rover Curiosity conducts high-precision in situ chemical measurements of rocks and regolith. Target surfaces are not always flat and thus can pose issues for interpretations that assume such. Here, we investigate when variable target relief is an important effect to consider for APXS targets. We provide operational recommendations on how to most efficiently study targets of significant changes in surface relief with the rover-arm-mounted APXS and Mars Hand Lens Imager camera. Additionally, we deconvolve the chemistry of heterogeneous targets of significant vertical relief encountered along Curiosity’s traverse, providing the chemical composition of visible endmembers in the process. Specifically, presented here are the deconvolved end-member compositions of two recent targets. The first is a manganese-rich, calcium-rich, and zinc-rich dark-toned vein at Garden City that is chemically and visually unique compared with the intermixed light-toned Ca-sulfate-dominated vein. The other target is a weathered Mg-sulfate-rich nodule that is unique compared with a previously encountered nodule that had significant nickel enrichment. The distinctly different chemistry both at Garden City and with the Mg-sulfate-rich nodules along the traverse provides further evidence for either multiple fluid events or an evolving fluid on the surface of ancient Mars. © 2017 John Wiley & Sons, Ltd.
2.2.2 Introduction and motivation

Onboard NASA’s Mars Science Laboratory (MSL) rover, Curiosity, are two robotic-arm-mounted instruments contributing to the mission’s quest to identify and investigate potential records of past habitable environments on Mars [46]. Through complementary particle-induced X-ray emission and X-ray fluorescence excitation methods, the Alpha Particle X-ray Spectrometer (APXS) conducts high-precision in situ measurements of Martian rocks and regolith. Concentrations of major, minor, and trace rock-forming elements measured by the APXS are determined for a circular field of view (FOV) that is typically 15-25 mm in diameter. Gellert et al. [5] provide a detailed description of the predecessor Mars Exploration Rover (MER) APXS instrument, the APXS method, and the approach to data analysis. Also mounted at the end of Curiosity’s arm is the Mars Hand Lens Imager (MAHLI). This color camera can provide images of the Martian surface over a range of working distances from 2.1 cm to infinity. At the minimum distance, images have a resolution of approximately 13.9 μm/pixel. The majority of APXS observations are accompanied by MAHLI images acquired from a 6.9-cm working distance, providing a standard resolution of approximately 31 μm/pixel [37, 38, 47].

Remote robotic X-ray spectroscopy on the surface of Mars has little or no sample preparation, leading to non-ideal sample geometry and heterogeneity within samples due to the nature of robotic spacecraft operations. This results in targeted samples that are often a mixture of several distinct compositions such as a millimeter-wide or centimeter-wide vein (mineralized fracture fill) cutting across a dust-covered bedrock target. While Curiosity is equipped with a wire brush (Dust Removal Tool, DRT) [46] to remove the global Martian dust that can cover targets of interest, [29, 20, 30] not all targets are suitable for brushing - unconsolidated particles such as an eolian sand deposit. Additionally, the robotic arm may not be able to position the DRT to brush the target because of surface roughness, an obstruction, or arm positioning geometry. Even for targets that are suitable for brushing, residual dust typically remains even after brushing.

Sample heterogeneity and variable geometry are important considerations for interpreting APXS spectra. The general approach for an APXS analysis assumes a homogeneous
sample, where sample surface relief can be ignored. On Mars, the effect of variable relief can be minimized by selecting flat targets. MAHLI images of compositionally heterogeneous targets can be used to address inhomogeneity within an APXS target. VanBommel et al. [21] assumed negligible target relief in the measurements investigated and deconvolved the chemical composition of distinct visual endmembers (VEs) within the FOV of the APXS, mitigating uncertainty in the robotic positioning of the APXS in the process.

The contribution to a spectrum of a small area within the FOV of the APXS varies both radially and vertically. The relative contribution to the spectrum of an area near the edge of the APXS FOV is significantly less than that directly below the center of the APXS sensor head, where the detector is situated [21]. Vertically, peak areas decrease with increasing standoff as the isotropic emission and decreasing detector solid angle outcompete the increase in FOV size associated with a larger standoff. In accordance with accepted terminology on both MER and MSL missions, standoff is a technical term used to describe the average separation between the targeted surface and instruments like the APXS. On Curiosity, the APXS standoff is measured between the target and a contact-sensing plate 18 mm from the instrument face. Additionally, the term raster describes multiple laterally offset measurements closely surrounding a primary target [21].

From a given APXS spectrum, the apparent standoff is empirically determined during on-the-ground analysis. The apparent standoff is calculated using a relative (to standard in-contact deployment) count rate and considers the decay of the instrument’s curium sources. This permits retroactive estimation of the instrument standoff, in a manner that complements the information given by the rover’s robotic arm position encoders and the APXS contact sensor. This reliable and well-characterized vertical sensitivity is the basis for “proximity mode”, a technique used to sense the distance between the APXS and a target in a way that can be fed back into a control loop during arm placement. Proximity mode is used during certain deployments to prevent overdriving the instrument into loose, unconsolidated targets with mechanical properties that might not reliably trip the contact sensor. When operating in proximity mode, the rover arm is positioned well above (∼5 cm) the target, then advanced in small steps toward it. At each step, the APXS acquires a short (∼15 s) measurement and compares the overall count rate to a predefined threshold. The
result of this comparison is returned to the rover computer and used to determine whether another step should be taken. The confidence in instrument response that permits the use of proximity mode was characterized both in the laboratory and on Mars using both configurations (MER and MSL) of the APXS instrument. The relevant curve for the MSL APXS is illustrated in Fig. 2.13.

While VanBommel et al. [21] addresses heterogeneity, the targets under interrogation were still assumed to have no surface relief. We present an extension to that work that follows the same fundamental assumptions, in which

- each VE is chemically homogeneous;
- each VE is infinitely thick compared to the APXS sampling depth (on the order of less than a millimeter and further described in Gellert et al., [5], Rieder et al., [4] and Campbell et al. [11]);
- the contribution of a relative position within a FOV (r/R) is independent of FOV size; and
- the relative placement uncertainty of FOVs within a raster is negligible (i.e. the error is in the overall raster placement accuracy not relative placement of the FOVs).

By utilizing a three-dimensional (3D) surface model produced using MAHLI images, we no longer need to assume that the target is flat and furthermore can account for an off-normal deployment of the APXS. Thus, the following fundamental assumptions are also required:

- Radial sensitivity and vertical sensitivity are independent.
- We are forced to follow the perspective of MAHLI in rare cases where APXS and MAHLI are deployed at different angles and in turn visibly occluded portions of the MAHLI image could contribute to the APXS spectra.

The contribution of a small area in the APXS FOV, such as a single pixel in a MAHLI image documenting an APXS target, is a function of the APXS’s lateral sensitivity, $L(r)$,
and vertical sensitivity, $V(z)$ (Fig. 2.13), given by

$$S(r, z) = L(r) \cdot V(z). \quad (2.2)$$

To determine the relative abundance of each VE, $i$, in the FOV, we classify each pixel into $i$ orthogonal bins. Each bin is unique to a single VE such as, for example, a vein, a nodule, or dust. The abundance of each VE is then determined as a function of radius and surface relief with the sum over all VEs normalized to unity. That is, for a given VE, $i$, the raw contribution, $T(i)$, is given by

$$T(i) = \Sigma_{\text{pixels}} (S(r, z) \cdot B(i)), \quad (2.3)$$

where $B(i)$ is a logical (binary) matrix with a value of 1 for a given pixel that represents VE $i$. Thus, the relative contribution of each VE in the FOV, $P(i)$, is determined by

$$P(i) = \frac{T(i)}{\Sigma_j T(j)}, \quad (2.4)$$

and is analogous to “phase abundance” as used in VanBommel et al. [21] permitting the same endmember minimization algorithm to be utilized.

To generate a 3D surface mesh, we use MAHLI focus merge products. MAHLI focus merge products are produced from a stack of images acquired at different focal points, while the camera is held at a single position. Instrument software identifies the position for each pixel that has the best focus and merges these portions into a single best-focus image. The accompanying metadata can be interpreted as an 8-bit/pixel monochromatic image (archived under the term range map), which, through calibration, [37] corresponds to the relative relief of the target. The MAHLI focus merge relief product and its color counterpart can then be paired to produce a color 3D surface relief model of the target with sub-millimeter vertical resolution, sufficient for the purposes of this study. This method of relief model generation comes with the added benefit of not having to add extra robotic arm movements in Curiosity’s operational plan - as would be the case with stereo imaging - because it is standard practice [47] for MAHLI to document APXS targets from a similar
perspective each time. Furthermore, a 3D mesh provides the added benefit of being able to improve localization of APXS rasters in three dimensions, including possible off-normal deployments. Localization is the process whereby the APXS FOV position on a given target is inferred through chemical correlations thus reducing the uncertainty that arises from deploying using a robotic arm (Fig. 2.14). Typically, APXS and MAHLI are within several millimeter of the planned target but may themselves be separated by 4-5 mm [21]. While a surface mesh can be generated from Curiosity’s other cameras via stereo imaging [39] - as is used for initial APXS and MAHLI targeting - MAHLI focus merge products are preferred for APXS investigations because they provide much more precision and a similar viewing geometry perspective to the APXS sensor head.

With the ability to model APXS observations in a 3D environment, we investigate via simulation when the effects of target relief, as pertinent to interpreting APXS data, [40] are relevant. Furthermore, we present an extension to the method of VanBommel et al., [21] applied to physical targets interrogated on Mars. As MAHLI focus merge products are not always acquired, this study provides operational guidance for the purpose of APXS VE chemistry deconvolution, potentially freeing up data transmission bandwidth and rover resources when MAHLI focus merge products are not required.

2.2.3 Simulations

Simulations determined the relative effect of surface relief in APXS data. For simplicity, the simulations assumed a cylinder structure with variable diameter, height, and position within the circular APXS FOV. The importance of considering variable surface relief will also depend on the chemical gradient between the VEIs. For this reason, the simulated results are expressed as a ratio of the cylinder’s contribution to a spectrum using a flat surface relief model (FM, \(V(z) = 1\)) to that of the cylinder’s contribution to a spectrum in a model where relief is considered (TM). That is, we are comparing how much of a spectrum comes from the cylinder structure when the target is assumed flat with how much comes from the cylinder structure when its surface relief is considered.

We first investigate the effects when the center of the APXS FOV and the cylinder are co-aligned. Deployment was simulated at 0 mm standoff with respect to the top of the cylinder.
Note that targeting using the robotic arm on Curiosity is prone to both vertical (normal to the sample surface) and lateral (parallel to the sample surface) uncertainty. While the lateral uncertainty is typically small (order of 5-10 mm [33]), this length scale does result in a considerable change in the APXS instrument’s radial sensitivity illustrated in Figure 2.13 of VanBommel et al. [21]. Instances do occur on Mars in which a structure is laterally smaller than the APXS contact sensor opening and has significant vertical relief. In these cases, deploying the APXS to contact is avoided to prevent instrument face contamination or damage, opting instead to hover or forgo the measurement altogether.

Figure 2.15 illustrates the observed ratio of FM to TM. A white curve outlines the 0.95 ratio contour, where, if assumed flat, the cylinder VE will contribute 95% to a spectrum compared with when proper surface relief is considered. The largest deviations between FM and TM arise with cylinder diameters that occupy a fraction of the APXS 15-mm diameter in-contact FOV (white vertical line). As diameter increases to approximately 10 mm, the difference between FM and TM decreases, approaching 5%, as only the outer-most portion of the APXS FOV is interrogating the background VE. These extremities of the APXS FOV have minimal contribution to a spectrum, resulting in FM offering a close approximation to TM.

Next, the diameter of the cylinder was fixed as we investigated the more-likely Mars scenario of a non-aligned APXS deployment. Cylinder height was varied from 5 to 15 mm as an anticipated range for relevant Mars targets. Once again, we compare FM with TM as a ratio of the relative cylinder contribution to the spectrum. A dashed line illustrates a ratio of 0.95, while the different colors correspond to the labeled cylinder height.

Figure 2.16(a) illustrates a simulation of a 15-mm diameter cylinder. A 5% difference in the contribution between FM and TM arises at an offset of around 4-5 mm - the center of the APXS FOV is still on the cylinder but nearing the edge. An offset of 4-5 mm is important as it is on the scale of arm placement accuracy, [33] and a 4- to 5-mm discrepancy is also commonly observed during tool changes (rotations of the robotic arm turret to position another tool or instrument) with the rover arm [21].

Figure 2.16(b) illustrates the results of simulating a 10-mm diameter cylinder. FM deviates from TM even when the APXS FOV is aligned with the center of the cylinder.
As the APXS FOV is not completely filled by the cylinder, this is anticipated and also captured by Fig. 2.15. A deviation of 5% or more occurs within the first few millimeter of misalignment between the APXS FOV and the cylinder center. In the case of a 4- to 5-mm misalignment, FM would result in a cylinder VE contribution to a spectrum 50-80% that of TM. While not common on Mars, structures similar to a 10-mm diameter cylinder with an aspect ratio of approximately 1 have been interrogated, the results and implications discussed later.

Uncertainty in placing arm-mounted instruments like the APXS will result in offsets between the APXS FOV and the planned target [21]. Figure 2.15 illustrates that provided the target fills a significant portion and is aligned with the center of the APXS FOV, the deviation between FM and TM will be negligible. As misalignment increases, the deviation of FM from TM is acceptable provided the cylinder diameter is sufficiently wide. The most significant faults with the FM assumption arise when the APXS is deployed, and the center of the FOV is around a sharp change in surface relief and VE - like at the edge of the hypothetical cylinder. In these instances, depending on the height of the feature, the deviation of FM from TM in terms of cylinder contribution to the spectrum can exceed 20-30%. If the chemical composition difference between the raised feature and the background endmembers is subtle, deconvolution of the feature’s unique chemical composition from the background may be inconclusive if negligible relief is assumed.

2.2.4 Application on Mars

Investigating primarily sedimentary rocks [48] in northern Gale Crater on Mars, Curiosity’s APXS has measured science targets with centimeter-scale surface relief. VanBommel et al. [21] deconvolved the unique chemistry of a nodule encountered by Curiosity, providing constraints on an ancient diagenetic fluid from which the feature precipitated. This feature, first studied on Martian day (sol) 767 and named Morrison, has a dominant lateral scale with only small-scale and gradual variations in surface relief. Figure 2.17(a) illustrates this target with the blue line corresponding to the cross-section plotted in Fig. 2.17(b). We conduct the same analysis as reported in VanBommel et al. [21] considering now the effects of target relief. Table 2.5 captures the chemical composition of the deconvolved Morrison
feature VE as previously reported (FM) as well as when considering relief (TM). FM is a valid approximation as both analyses are well within uncertainty. This behavior is expected because of the small-scale changes in surface relief resulting in the feature’s contribution to a spectrum, $P(i)$, deviating by a maximum of 3% absolute between FM and TM as displayed in Table 2.6.

In 2015, the Curiosity team interrogated a collection of erosion resistant, protruding, light-toned and dark-toned veins at the field site called Garden City starting on sol 930. Nine APXS measurements of this feature were performed in close proximity to each other and given the names Alvord Mountain (spots 1 through 7), Indianola, and Coalville. These observations were specifically targeted to investigate each of the light-toned vein VE and dark-toned vein VE. Furthermore, a varying mix of the light-toned and dark-toned veinVEs was also targeted to provide sufficient gradient for the deconvolution. Figure 2.18(a) illustrates a MAHLI mosaic of the region studied by APXS, with the blue line representing the cross-section transect illustrated in Fig. 2.18(b). For a MAHLI-based 3D mesh of the area to be generated, the MAHLI focus merge monochromatic images were mosaicked, and the implied relative relief was scaled appropriately in each of the original images. A portion of the generated 3D product is shown in Fig. 2.18(c). The method described in VanBommel et al. [21] was once again utilized while considering the variable surface relief and its effect. Furthermore, by using the 3D mesh environment, it was possible to model the APXS measuring normal to the surface (nTM) in each instance. We first compare FM with TM for both the light-toned (Table 2.7) and dark-toned (Table 2.8) vein material VEs. Table 2.9 provides the results when comparing modeling APXS deployment normal to the surface (nTM) versus that of APXS deployed co-aligned with MAHLI (TM).

For the Garden City targets, there is little deviation in the deconvolved chemical composition between the FM and TM models because of the gradual and small slope in relief compared with the size of the APXS FOVs (15-20 mm). Thus, not unexpectedly, modeling the APXS normal to the surface (nTM) rather than co-aligned with the MAHLI images (TM) also resulted in agreement between the two models.

Deconvolution of the two phases that make up the Garden City targets indicates that the dark material (Table 2.8) is compositionally distinct from the white Ca-rich and S-rich
phase (Table 2.7). This definitively enhances geologic interpretations for the veins, as the dark material is rare [49] and the white material (Ca-sulfate) is common [50] in Gale Crater. Two different fluid compositions are indicated for each of the vein precipitates, consistent with a varied fluid history.

Later in the mission, Curiosity encountered a flattened cylindrical-shaped nodule on sol 1277, named Sperrgebiet, which had weathered out of a sandstone. Sperrgebiet is a physical example of what was presented in our preceding simulations. Figure 2.19(a) is a MAHLI image of the feature with the blue line corresponding to the cross-section shown in Fig. 2.19(b). Like Morrison, ancient diagenetic fluids likely precipitated the approximately 11.5-mm-diameter, 8-mm-tall nodule. This target is analogous to the 10-mm-diameter simulation scenario, and thus, surface relief should be considered to properly deconvolve the chemistry of the nodule VE from the surrounding bedrock VE. MAHLI generated a MAHLI focus merge product, from which the monochromatic range map, Fig. 2.19(c), facilitates the generation of the 3D mesh illustrated in Fig. 2.19(d).

Following VanBommel et al. [21] once again, we deconvolved the composition of the nodule VE from that of the background bedrock VE both when considering only the radial sensitivity of the APXS (FM) and also when considering both radial and vertical sensitivity (TM). The results are directly compared in Table 2.10. Due to the targeting of the three APXS FOVs on the nodule, the contribution of the nodule VE had only a small gradient ranging from 60% to 70% for TM and from 47% to 55% for FM. This difference of approximately 15% absolute is responsible for the deviation observed in Table 2.10. In terms of the preceding simulations, the deviation is comparable with the 10-mm curve in Fig. 2.16(b) and an offset of 2-3 mm between the center of the APXS FOVs and the center of the Sperrgebiet nodule, as was planned by the science and operations team.

Our analysis confirms an important contrast between Sperrgebiet and Morrison because of the difference in Ni content. Morrison is highly enriched in Ni, a common 2+ cation trace element substitution in Mg-sulfates, [51] whereas Sperrgebiet is not enriched in Ni. The two features, therefore, precipitated from fluids with different trace element concentrations either at different times or from an evolving fluid [52].
2.2.5 Conclusions and recommendations

The chemical deconvolution of distinct VEs has proven fruitful on a number of occasions for both active NASA Mars rovers, Curiosity and Opportunity [21, 53]. The ability, on the MSL Curiosity rover, to compensate for irregular surface relief efficiently with MAHLI focus merge products increases the confidence in results for these unique targets without adding operational complexity (in the form of extra robotic arm motions and operational duration) to Curiosity’s workload. The simulations herein and study of the features of interest provide a better understanding of cases for which knowledge of centimeter-scale to sub-millimeter-scale surface relief is important. From a tactical operations planning perspective, they also provide guidance as to when the non-standard MAHLI focus merge data products should be acquired by Curiosity’s operations team, consuming plan time and generating data to transmit only when necessary.

This capability extends the scientific return of APXS measurements and emphasizes the ability to precisely measure the composition of the less-than-ideal targets of interest encountered by rovers on the surface of Mars with the APXS. To that end, the work of VanBommel et al. [21] and the general assumption of flat surface relief used in the APXS method, is sufficient in the vast majority of targets examined by Curiosity’s APXS on Mars. However, creating 3D models of APXS deployments, where the data are available, helps to improve our interpretation of the apparent standoff. Additionally, by modeling these deployments, we gain information that can be used to adjust subsequent deployments and further improve APXS localization.

The chemical deconvolution of the targets of considerable surface relief presented herein provides yet more evidence for a complex ancient Mars fluid environment. Possible further application also exists with the MER rover Opportunity in regard to the hematite spherules encountered at its landing site, Eagle Crater, on Meridiani Planum [2]. Despite not having a MAHLI-like 3D model for an APXS perspective, the spherical shape and diameters of around 5 mm resemble the cylinder-like situation modeled here and prompts further study.
2.2.6 Acknowledgements

This work has been supported by the Canadian Space Agency (CSA) under contract 9F052-14-0592. The MSL APXS is financed and managed by the CSA. MacDonald Dettwiler and Associates was the primary contractor to build the instrument. Funding for the APXS science team is provided by the CSA and NASA. MAHLI development, operations, and data archiving were supported by NASA via Caltech-JPL subcontracts to Malin Space Science Systems. Much appreciation goes to NASA/JPL for their support, dedication, and invaluable expertise during development and operations.
2.2.7 Tables

Table 2.5: Deconvolved chemical composition of the Morrison nodule visual endmember when considering target surface relief (TM) and that of the previously published VanBommel et al. [21] concentrations that used a flat target assumption (FM). The small-scale and smooth changes in relief result in an agreement between the models. Values are expressed in weight percent unless otherwise specified. Errors in TM correspond to a change in concentration that increases the $\chi^2$ of the nonlinear least-squares fit by 1.0 and differ in calculation slightly from those in FM.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
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<td>2.49±0.14</td>
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<tr>
<td>MgO</td>
<td>7.90±0.15</td>
<td>7.7±0.15</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.87±0.20</td>
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</tr>
<tr>
<td>SiO$_2$</td>
<td>43.57±0.66</td>
<td>43.97±0.27</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>1.08±0.05</td>
<td>1.09±0.06</td>
</tr>
<tr>
<td>SO$_3$</td>
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<td>11.83±0.13</td>
</tr>
<tr>
<td>Cl</td>
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<td>0.65±0.02</td>
</tr>
<tr>
<td>K$_2$O</td>
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<td>0.73±0.02</td>
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<tr>
<td>CaO</td>
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<tr>
<td>TiO$_2$</td>
<td>0.92±0.10</td>
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<td>Cr$_2$O$_3$</td>
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<tr>
<td>MnO</td>
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<td>0.33±0.01</td>
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<td>FeO</td>
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<td>Ni(µg/g)</td>
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<td>Zn(µg/g)</td>
<td>2345±10</td>
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<tr>
<td>Br(µg/g)</td>
<td>164±5</td>
<td>142±5</td>
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Table 2.6: Spectrum contribution of the Morrison nodule visual endmember (VE) considering variable target surface relief (TM) compared with that when neglecting surface relief (FM). The coverage gradient across all five unique spots (A-D and Center) on the Morrison target permits the deconvolution of nodule VE chemistry from the background host rock VE despite a similar chemistry. Furthermore, the gradual and small-scale relief changes in the feature result in minor, up to 3% absolute, differences in nodule VE contribution to a spectrum between the two models. This supports FM as an appropriate approximation, reflected in the chemistry extracted and presented in Table 2.5.

<table>
<thead>
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<tr>
<td>Spot A</td>
<td>53%</td>
<td>55%</td>
</tr>
<tr>
<td>Spot B</td>
<td>29%</td>
<td>32%</td>
</tr>
<tr>
<td>Spot C</td>
<td>19%</td>
<td>19%</td>
</tr>
<tr>
<td>Spot D</td>
<td>29%</td>
<td>30%</td>
</tr>
<tr>
<td>Center</td>
<td>74%</td>
<td>76%</td>
</tr>
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</table>
Table 2.7: Chemical composition of the light-toned vein material visual endmember considering (TM) and neglecting (FM) the surface relief of the Garden City Alpha Particle X-ray Spectrometer targets. Values are expressed in weight percent unless otherwise specified. Errors correspond to a change in concentration that increases the $\chi^2$ of the nonlinear least-squares fit by 1.0.

<table>
<thead>
<tr>
<th></th>
<th>TM</th>
<th>FM</th>
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</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>1.26±0.04</td>
<td>1.28±0.03</td>
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<tr>
<td>MgO</td>
<td>3.49±0.11</td>
<td>3.61±0.13</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.19±0.13</td>
<td>2.39±0.14</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>9.81±1.12</td>
<td>10.88±0.52</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.56±0.05</td>
<td>0.57±0.04</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>47.92±1.83</td>
<td>46.01±2.09</td>
</tr>
<tr>
<td>Cl</td>
<td>0.56±0.06</td>
<td>0.64±0.06</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.10±0.02</td>
<td>0.10±0.01</td>
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<tr>
<td>CaO</td>
<td>30.6±0.48</td>
<td>30.19±0.68</td>
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<tr>
<td>TiO$_2$</td>
<td>0.11±0.01</td>
<td>0.13±0.01</td>
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<tr>
<td>Cr$_2$O$_3$</td>
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<td>0.10±0.01</td>
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<tr>
<td>MnO</td>
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<td>0.03±0.07</td>
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<tr>
<td>FeO</td>
<td>3.22±0.46</td>
<td>3.96±0.52</td>
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<tr>
<td>Ni(μg/g)</td>
<td>19±32</td>
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<tr>
<td>Zn(μg/g)</td>
<td>49±111</td>
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<tr>
<td>Br(μg/g)</td>
<td>52±39</td>
<td>78±17</td>
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Table 2.8: Chemical composition of the dark-toned vein material visual endmember considering (TM) and neglecting (FM) the surface relief of the Garden City Alpha Particle X-ray Spectrometer targets. Values are expressed in weight percent unless otherwise specified. Errors correspond to a change in concentration that increases the $\chi^2$ of the nonlinear least-squares fit by 1.0.

<table>
<thead>
<tr>
<th></th>
<th>TM</th>
<th>FM</th>
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<tbody>
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<td>$\text{Na}_2\text{O}$</td>
<td>1.49±0.03</td>
<td>1.49±0.03</td>
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<td>$\text{MgO}$</td>
<td>6.16±0.10</td>
<td>6.15±0.07</td>
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<td>$\text{Al}_2\text{O}_3$</td>
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<td>5.69±0.10</td>
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<td>$\text{SiO}_2$</td>
<td>34.94±1.32</td>
<td>34.86±1.04</td>
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<td>$\text{P}_2\text{O}_5$</td>
<td>0.91±0.04</td>
<td>0.91±0.03</td>
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<tr>
<td>$\text{SO}_3$</td>
<td>6.43±1.86</td>
<td>6.65±1.66</td>
</tr>
<tr>
<td>$\text{Cl}$</td>
<td>1.88±0.04</td>
<td>1.86±0.03</td>
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<tr>
<td>$\text{K}_2\text{O}$</td>
<td>0.10±0.01</td>
<td>0.10±0.01</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>23.09±0.44</td>
<td>23.17±0.54</td>
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<tr>
<td>$\text{TiO}_2$</td>
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<td>0.58±0.02</td>
</tr>
<tr>
<td>$\text{Cr}_2\text{O}_3$</td>
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<td>0.23±0.01</td>
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<td>$\text{MnO}$</td>
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<td>1.01±0.05</td>
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<tr>
<td>$\text{FeO}$</td>
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<td>16.85±0.34</td>
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<tr>
<td>$\text{Ni}(\mu\text{g/g})$</td>
<td>662±30</td>
<td>652±22</td>
</tr>
<tr>
<td>$\text{Zn}(\mu\text{g/g})$</td>
<td>2438±78</td>
<td>2397±64</td>
</tr>
<tr>
<td>$\text{Br}(\mu\text{g/g})$</td>
<td>266±21</td>
<td>258±10</td>
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Table 2.9: Chemical composition of the dark-toned vein material visual endmember comparing modeling deployment aligned with Mars Hand Lens Imager (TM) and normal to target surface (nTM). Values are expressed in weight percent unless otherwise specified. Errors correspond to a change in concentration that increases the $\chi^2$ of the nonlinear least-squares fit by 1.0.

<table>
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<th>nTM</th>
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<tr>
<td>Na$_2$O</td>
<td>1.49±0.03</td>
<td>1.51±0.03</td>
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<td>MgO</td>
<td>6.16±0.10</td>
<td>6.26±0.08</td>
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<td>Al$_2$O$_3$</td>
<td>5.74±0.13</td>
<td>5.85±0.11</td>
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<td>SiO$_2$</td>
<td>34.94±1.32</td>
<td>36.00±1.22</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.91±0.04</td>
<td>0.94±0.04</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>6.43±1.86</td>
<td>5.02±1.49</td>
</tr>
<tr>
<td>Cl</td>
<td>1.88±0.04</td>
<td>1.92±0.04</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.10±0.01</td>
<td>0.11±0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>23.09±0.44</td>
<td>22.66±0.49</td>
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<tr>
<td>TiO$_2$</td>
<td>0.58±0.02</td>
<td>0.61±0.02</td>
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<tr>
<td>Cr$_2$O$_3$</td>
<td>0.23±0.01</td>
<td>0.24±0.01</td>
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<tr>
<td>MnO</td>
<td>1.01±0.05</td>
<td>1.04±0.04</td>
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<td>17.47±0.41</td>
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<tr>
<td>Ni(μg/g)</td>
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<td>Zn(μg/g)</td>
<td>2438±78</td>
<td>2520±85</td>
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<tr>
<td>Br(μg/g)</td>
<td>266±21</td>
<td>328±25</td>
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Table 2.10: Comparison of deconvolved chemical composition of the Sperrgebiet feature visual endmember considering (TM) and ignoring (FM) the relief of the feature. A comparison of the deconvolved chemistry in each scenario emphasizes the importance of considering relief for this specific target. Most notably, the difference in MgO and SO$_3$ concentrations is critical for estimating sulfate addition (relative to the host mafic sandstone) that formed the nodule. This implies a deconvolved nodule composition (in TM) that is a mixture of roughly 85% host bedrock and 15% MgSO$_4$. Also noticeable is a decrease in Ti and Cr, two usually less-soluble elements, in the feature. Values are expressed in weight percent unless otherwise specified. Errors correspond to a change in concentration that increases the $\chi^2$ of the nonlinear least-squares fit by 1.0.

<table>
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<tr>
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<td>Na$_2$O</td>
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<tr>
<td>MgO</td>
<td>17.47±0.35</td>
<td>13.32±0.43</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>5.01±0.15</td>
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<td>P$_2$O$_5$</td>
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<td>SO$_3$</td>
<td>36.15±1.17</td>
<td>22.19±1.53</td>
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<td>Cl</td>
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<tr>
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<td>Cr$_2$O$_3$</td>
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<td>Zn(μg/g)</td>
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<tr>
<td>Br(μg/g)</td>
<td>619±10</td>
<td>533±20</td>
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</table>
2.2.8 Figures

Figure 2.13: Alpha Particle X-ray Spectrometer relative count rate response curve reproduced from Mars measurements, laboratory testing, and Gellert et al., [5] for the Mars Science Laboratory instrument. As a quick estimate, a spectrum acquired at 10 mm standoff has a count rate of half that at contact and approximately twice as much as 20 mm standoff. Standoff is defined from a contact-sensing plate situated 18 mm in front of the instrument (Fig. 2.14).
Figure 2.14: Mastcam-34 mosaic (sequence mcam00906) from sol 168 showing the Alpha Particle X-ray Spectrometer instrument head, emphasized on the right, deployed for measurement on a rock surface. For scale, the turret is approximately 60 cm in diameter, whereas the drill bit is 1.6 cm in diameter.

Figure 2.15: Relative contribution of a cylinder to a Mars Science Laboratory Alpha Particle X-ray Spectrometer (APXS) spectrum with a flat (negligible) surface relief assumption (FM) compared with the contribution of a cylinder to a spectrum when relief is considered (TM). The color corresponds to the ratio FM/TM for a given cylinder diameter and height assuming the APXS field of view is co-aligned with the center of the cylinder. The white, curved line corresponds to the different cylinder heights and diameters where the cylinder contributes 95% to a spectrum under the flat assumption compared with the cylinder contribution with surface relief considered. The white vertical line corresponds to the in contact APXS field of view diameter. In both FM and TM, APXS is simulated deploying to “contact” at the top of the cylinder, regardless of cylinder dimensions, and co-aligned with its center. The effect of sample-instrument separation is <5% for the range of appreciable target dimensions deemed safe for interrogation with the APXS.
Figure 2.16: Relative contribution of a cylinder to a spectrum with a flat surface assumption (FM) compared with the contribution of a cylinder to a spectrum when surface relief is considered (TM). Cylinder diameter locked to (a) 15 mm and (b) 10 mm (approximately that of a target encountered on Mars). Colored lines correspond to different cylinder heights. At approximately 5 mm offset between the Alpha Particle X-ray Spectrometer (APXS) field of view (FOV) center and the cylinder center, a 15-mm diameter cylinder will contribute 95% to a spectrum in FM compared with TM. A 5-mm offset is on the order of Curiosity’s arm accuracy [33]. In the 10-mm diameter scenario, because of a cylinder diameter smaller than the APXS FOV, the deviance between FM and TM will exceed 5% even when the APXS and cylinder are co-aligned. A 5-mm offset, as is on the order of Curiosity’s arm accuracy, [33] can result in the 10-mm diameter cylinder contributing 60-80% under FM compared with TM. The cylinder does not contribute to the APXS FOV when exceeding an offset of 15 and 12.5 mm in (a) and (b), respectively.
Figure 2.17: (a) Mars Hand Lens Imager view (image ID: 0767MH0003630010300137C00) of the Morrison target, the globular feature in the center of the frame transected down the middle by the blue line, after it was brushed by the rover’s Dust Removal Tool. The target was fully shadowed by the robotic arm hardware. The image covers an area approximately 5 cm by 3.7 cm. The blue line corresponds to the cross-section illustrated in (b). The feature is significantly enriched in Mg-Ni-sulfate compared with the surrounding bedrock [21].

Figure 2.18: (a) Mosaic of Mars Hand Lens Imager (MAHLI) images covering the Garden City Alpha Particle X-ray Spectrometer (APXS) raster investigation site. Image covers an area approximately 8.5 cm by 7 cm. The blue line corresponds to the cross-section illustrated in (b); (c) represents a portion of a 3D model of the Garden City APXS raster area generated from a MAHLI focus merge product mosaic. Image IDs: 0935MH0001700000303353R00, 0935MH0001700000303355R00, 0935MH0001700000303357R00, 0935MH0001700000303365R00, 0938MH0002650000303537R00, 0935MH0001700000303356S00, 0935MH0001700000303362S00, 0938MH0002650000303536S00, and 0938MH0002650000303538S00.
Figure 2.19: (a) Mars Hand Lens Imager (MAHLI) image of the Sperrgebiet nodule. Image covers an area approximately 5 cm by 3.7 cm. The blue line corresponds to the cross-section illustrated in (b) generated from the monochromatic 8-bit/pixel MAHLI focus merge range map product in (c). This facilitates the calculation of the relative vertical relief through calibration and in turn the generation of the 3D model in (d). Image IDs: 1278MH0001660010404732C00, 1278MH0001700000500006S00, and 1278MH0001700000500005R00.
Chapter 3

Submitted Article

Included in this chapter is a submitted manuscript. Formatting, as well as figure, table, and reference numbers have been changed to be consistent throughout this thesis. Figures and table locations within deviate from the submitted manuscript. In-line reference formatting matches submitted journal requirements. Reference list at the end of the manuscript listed in alphabetical order per journal requirements, with thesis reference numbers and format included in front of each. The reader is strongly encouraged to refer to the eventual published manuscript where final reviewer suggestions and editorial changes will be captured.

Seasonal atmospheric argon variability measured in the equatorial region of Mars by the Mars Exploration Rover Alpha Particle X-ray Spectrometers: Evidence for an annual argon-enriched front


3.1 Abstract

The Mars Exploration Rover Opportunity (MER-B) has been exploring the surface of Mars since landing in 2004. Its Alpha Particle X-ray Spectrometer (APXS) is primarily used to interrogate the chemical composition of rocks and soil samples in situ. Additionally, the
APXS has measured the atmosphere of Mars with a regular cadence, monitoring the change in atmospheric argon density. Atmospheric measurements with the MER-B APXS span over six Mars years providing an unprecedented level of statistics for careful study of the ubiquitous APXS spectral background. Several models were applied to high-frequency long-duration Spirit rover atmospheric APXS measurements. The most-stable model with the least uncertainty was applied to the MER-B data set. Seasonal variation of 10-15% in equatorial atmospheric argon density was observed - in agreement with existing literature and global climate models (GCMs). Unseen in previous work and GCMs, an abrupt deviation from the model-predicted annual mixing ratio was measured by the MER-B APXS around $L_s$ 150. The sharp change, $\sim$10% over $10^6$ $L_s$, provides strong evidence for a northward migrating front, enriched in argon, sourced from the south pole at the end of southern winter. A similar weaker front is possibly observed around $L_s$ 325, sourced from the northern polar region.

3.2 Introduction

In January 2004, twin rovers Spirit and Opportunity landed on opposite sides of Mars as part of the Mars Exploration Rover (MER) mission [Arvidson et al., 2006; Squyres et al., 2006]. Included on each rover as part of the Athena science payload was an Alpha Particle X-ray Spectrometer (APXS) [Rieder et al., 2003]. The APXS utilizes $^{244}$Cm sources to generate alpha particles and X-rays that in turn interrogate samples via X-ray excitation [Rieder et al., 2003; Gellert et al., 2006]. While the use of the APXS is focused on determining the chemistry of rocks, soils, and, in general, solid samples deployed into close contact [Rieder et al., 2003], measurements of the Martian atmosphere have been acquired with a semi-regular cadence [Arvidson et al., 2011]. APXS atmospheric interrogations measure the abundance (atomic density) of argon in the Martian atmosphere, independent of the other constituents. Atmospheric measurements with the Opportunity rover (MER-B) APXS were attempted every two to four weeks over several Martian years. The APXS on Spirit (MER-A) followed a similar cadence prior to being stuck on sol (Martian days since landing) 1892. Spirit conducted long-duration atmospheric measurements with the APXS almost daily over the
course of several weeks while unable to move.

The atmosphere of Mars is dominated by CO$_2$ (96\% v/v) with minor amounts of Ar (<2\%), N$_2$ (<2\%) and other trace gases [Mahaffy et al., 2013]. Over the course of the Martian year, much of the atmosphere accumulates as frozen CO$_2$ at the winter pole, especially during the longer southern winter [Sprague et al., 2004; 2007; 2012; Arvidson et al., 2011].

In this work we discuss the atmospheric spectra collected by the MER APXS instruments. We present instrument design considerations that could impact the count rate for argon. The high-quality measurements on Spirit were used to demonstrate the reliability of the results over short timescales. Several analysis models were tested to determine the method of estimating relative argon density variation with the least error. We illustrate the timing and magnitude of the variation in argon is largely aligned with complementary observations made by previous (Viking 1, Viking 2) and active (Curiosity) surface pressure monitoring instruments and global climate models (GCMs). A short-lived argon enrichment is observed for the first time and is interpreted as evidence for a front enriched in non-condensable gases. In addition to demonstrating the precision of the APXS, even with sparse samples, the results herein provide ground truth data and insight for atmospheric modeling involving non-condensable gases on Mars.

### 3.3 APXS Instrument Operational Considerations

The MER APXS was optimized in design for and extensively calibrated with solid samples. While the Mars Pathfinder APXS calibration was performed with 8 mbar of Mars equivalent gas containing ~1\% argon, the MER calibration campaign, for simplicity, used a pure CO$_2$ atmosphere of 10 mbar. There have not been any calibration efforts of long-term gas measurements nor an absolute partial pressure calibration of the argon content. Laboratory measurements of solid samples in vacuum resulted in a <1\% increase in Cl peak area compared to measurements conducted under 10 mbar CO$_2$. Therefore, a change in atmospheric CO$_2$ abundance has a negligible effect on Ar count rates. There are several aspects in the MER APXS instrument design that may impact the absolute count rate. These are presented in this section. During MER calibration, every sample was typically measured
for a day in 15 minute intervals triggered by an external computer. Conditions, including pressure and temperature (-40°C), were kept constant during acquisition. Through this method, the instrument was found to run stable, with count rates well within one percent of each other. Small deviations are caused by an idiosyncrasy in that the lifetime of each spectrum is reported as a multiple of 10 seconds. The absolute lifetime is rather insensitive for solid samples because APXSoxide results are normalized to 100%. Absolute lifetime deviations of ∼10% would be equivalent to a change in distance to the sample on the order of a millimeter. The potential effects in the oxide results are therefore negligible.

Per design, the hardware timer for counting the lifetime of a spectrum is halted during the analysis of a single pulse sourced from either the X-ray or one of the two alpha particle channels. Additionally, there are other housekeeping tasks in the firmware where new acquisition is prohibited and the lifetime counter is paused. As determined during calibration, a typical processing time for each detected pulse is approximately 300 microseconds. This implies that a significant count rate in the alpha channels, which are known to be sensitive to light as well as radio-frequencies, could affect the live time of a measurement. Early morning atmospheric spectral acquisitions after sunrise show that the dead time increases dramatically and in turn impacts the X-ray count rate. While the dead time design should be robust against any reasonable level of noise, overwhelming noise can have significant impact. To exclude this impact on X-ray analyses of the atmosphere, measurements with alpha count rates exceeding 1.2 counts per second (cps) were excluded from the analysis. Any reasonable level of noise should not impact the frequency at which spectra are saved during a single commanded integration. Only the last spectrum acquired is shutdown by a command from the rover and therefore has a 10-second uncertainty.

Nominally, atmospheric APXS spectra are easily conducted with little resources required - a dedicated deployment of the IDD (Instrument Deployment Device, rover arm) is not necessary. The APXS instrument consumes approximately 3W of power and is able to operate while the rover CPU is inactive. Only 32 kBytes of data are produced, consisting of up to 12 new X-ray spectra of 512 channels acquired consecutively with a predetermined cycle time. However, for the Opportunity rover, additional considerations have to be taken into account for dedicated APXS atmospheric measurements. Since landing, an arm heater
is stuck on and consumes power whenever the temperature is below approximately -50°C. To overcome this significant nightly power drain, a mode called “deep sleep” was developed that removes the battery from the stuck heater and rover computer in the evening. After sunrise, the solar panels power on the rover and the battery is reconnected. This mitigation strategy makes APXS argon measurements very power intensive and limits the cadence of data taken. A “mini deep sleep” is often utilized, whereby the rover is powered off before midnight, allowing for 3 hours of good APXS data.

The rover now operates in RAM mode with the failure of the non-volatile flash RAM. While operating in RAM mode, all science data are stored only in RAM and lost upon powering down. Most data (e.g., images) are taken during the daytime and are downlinked to the orbiters in the late afternoon. APXS data, acquired in the evening after the orbiter pass(es), are saved on the rover but lost at the start of (mini) deep sleep. To mitigate this, a design feature of the APXS electronics is used that buffers the volatile 32 kByte RAM with a small battery inside the APXS main electronics. The rover powers on the APXS instrument prior to the orbital pass on a subsequent sol and retransmits the buffered data to the rover for downlink. Unique identifying numbers for each spectrum permit the separation of newly acquired data for analysis. The increased strain on the APXS was deemed scientifically worthwhile considering the added risk of a critical failure through an increase in operating time and power cycles.

### 3.4 Martian Atmospheric Measurements with the APXS

#### 3.4.1 APXS Atmospheric and Geologic Spectra

The APXS sensor head is lowered to near-contact with the target using the IDD to measure geologic samples. A spectrum is acquired by interrogating the sample with energetic alpha particles and X-ray radiation generated during the decay process of the six $^{244}$Cm sources. The characteristic and scattered X-rays are collected by a silicon drift detector (SDD), processed by onboard electronics, and tabulated in a histogram with bins (referred to as channels) corresponding to detected photon energy. Data are acquired over a pre-determined time period (integration time) during which the APXS saves spectra to its memory at
pre-defined intervals (cycle time) until the instrument is commanded to stop by the rover computer [Rieder et al., 2003; Gellert et al., 2006]. The MER APXS memory buffer can store 12 individual spectra within its memory buffer. With a few exceptions, it is convention within the APXS operations team to try to fill as many of the 12 spectral slots as possible during an integration to maintain the smallest temperature delta for each spectrum. This permits the data to be filtered, ultimately improving the spectrum resolution for final analysis. Instrument sequences are reusable and delivered based on desired cycle time, dictated in part by the total allocated integration time.

Elements in a spectrum, whether inherent to the sample, atmosphere, or rover hardware, present peaks at characteristic energies. The complementary use of both Particle-Induced X-ray Emission (PIXE), by way of emitted alpha particles, and X-ray Fluorescence (XRF), by way of Pu L X-rays, results in a smooth and strong sensitivity for elements of atomic number equal to sodium and above [Rieder et al., 2003; Gellert et al., 2006]. In geologic samples, a spectrum consists of several characteristic peaks inherent to the sample, including primary and secondary lines. In addition to these signals, Zr from the APXS collimator and Ar from the atmosphere increase the effective background in the appropriate energy region. There are also elastic and inelastic Pu L line scatter peaks above 12 keV.

With the exception of Ar, the Martian atmosphere is composed of elements the APXS cannot detect directly through characteristic peaks. Figure 3.1a compares a spectrum from a geological sample (blue) with a spectrum from the atmosphere of Mars (red). There is a noticeable difference in count rate as well as a bremsstrahlung background visible in the low-energy region of the atmospheric spectrum. A Zr peak (around channel 490) is present in both spectra. A detailed description of geologic sample spectra can be found in Rieder et al. [2003] and Gellert et al. [2006]. The majority of the argon signal comes from the 3 cm column of air between the APXS sensor head and the contact ring. A discussion of atmospheric spectral features follows in §3.4.3.

3.4.2 MER APXS Energy Calibration

An APXS X-ray spectrum consists of 512 discrete energy channels with engineering data occupying the first seven. The channel position of a detected peak of given energy is de-
pendent on the energy scale of the instrument [Gellert et al., 2006]. The energy for a given channel increases monotonically (gain - units eV/channel) with a near-zero energy at channel 0 (offset - units eV). The gain of a spectrum has a thermal response due to the signal processing amplifiers. The position of peaks within a spectrum would change considerably with temperature if left uncorrected. Correction is achieved by firmware within the APXS that uses an internal temperature sensor [Rieder et al., 2003; Gellert et al., 2006]. Temperature compensation parameters are included in the command set whenever the APXS instrument is integrating. Proper temperature compensation maintains spectrum resolution by avoiding excess peak broadening through a near-constant energy scale throughout the diurnal temperature cycle on Mars. Spectral sums are beneficial to improve statistics and reduce uncertainty especially in APXS atmospheric spectra. Stable peak positions are critical to maintaining peak shape and resolution when summing multiple spectra.

The peak positions of the 2.96 keV Ar K\textalpha\ peak and (15.77,15.69) Zr K\textalpha\(1,2) peak(s) in atmospheric spectra were fit with a least-squares Gaussian and linear background model. In Figure 3.2a there is a distinct dichotomy in gain between the shorter (30 and 40 minutes) and longer cycle times (60 and 90 minutes). As a result, an observed Zr K\textalpha\(1,2) peak position difference of approximately 5 channels (see Figure 3.2c) would significantly degrade the peak shape when summing spectra of both short and long cycle times. The effect is not as noticeable for the lower-energy Ar peak (order 1-2 channel shift, see Figure 3.2c, bottom). Sequence inspection confirmed different temperature stabilization was applied to the short cycle times and the longer cycle times - unique to the MER-B APXS. The offset was not dependent on cycle time (Figure 3.2b). The dichotomy in gain has no effect on the published analytical results of geologic samples where energy scale parameters are included as variables in the fit routine (described in detail by Gellert et al. [2006]).

Each spectrum underwent a linear transformation to achieve a consistent energy scale. Figure 3.2c illustrates the spectral sum for each of short and long cycle times. The different parameter sets would result in artificial peak broadening and a distortion of peak shape (increasing with energy) should spectra from short and long cycle times be summed together. Figure 3.2d illustrates the same summed spectra after a linear energy transformation correction is applied. These energy-corrected spectra are utilized in all relevant analyses that
3.4.3 Atmospheric Spectral Features

A few spectral features are apparent in a single atmospheric measurement (Figure 3.1a, red line). Zirconium lines from the collimator are visible at 2.01 keV (L line) as well as around 15.75 keV (Kα lines). The highest count rates are obtained in the argon Kα peak (2.96 keV). The argon Kβ peak (3.21 keV) is also visible. Frequently above the background, 6.40 keV Fe Kα and 8.05 keV Cu Kα peaks can be observed. The iron lines are likely associated with iron in the stainless steel source holder surrounding the detector. The copper lines come from copper in the copper-beryllium doors as well as from the rod/screw that the SDD sits on, intended as a heat sink for the not-used Peltier cooler. Other signals are visible when statistics are improved.

3.4.3.1 Atmospheric Summed Spectrum

Opportunity has collected more than 1,600 hours of good-resolution (2,232 hours total) APXS atmospheric spectra since sol 1000. This level of integration time provided excellent statistics to probe the ubiquitous spectrum background including signals that do not persist above the noise in an individual spectrum. Figure 3.1b illustrates the summed spectrum of all 1,600+ hours of good-temperature energy-normalized atmospheric spectra, with a least-squares fit similar to Gellert et al. [2006] applied.

The background in Figure 3.1b (green) includes alpha-induced bremsstrahlung radiation. A slowly varying linear background arises from incomplete energy dissipation (Compton scattering) of high energy photons and incomplete charge collection at edges within the SDD. Lines are visible at 13.53 keV due to Compton scattering and at 14.3 keV (Lα) arising from Pu L X-rays penetrating the instrument shielding and reaching the detector with cumulative count rates of approximately 7x10^{-3} counts per second (cps). This is not surprising given 10s of millions of Pu L X-rays are emitted per second by the APXS.

Characteristic peaks include the argon Kα and Kβ peaks with a combined peak area of approximately 0.2 cps. (Figure 3.1b, in red) The Ar Kα escape peak at 1.22 keV is not discernible in the spectrum but has an anticipated order of magnitude comparable to visible
higher energy peaks. The Zr L lines, around 2.01 keV, have peak areas typically around 0.025 cps. The broadness of the 15.7-15.8 keV Zr Kα peak is attributed to the convolution of the Kα1 and Kα2 peaks, with a combined peak area of around 0.13 cps. Accompanying the Fe and Cu Kα peaks visible in individual measurements are their associated Kβ peaks (7.05 and 8.94 keV). A faint aluminum peak at 1.49 keV appears above the bremsstrahlung-dominated background, associated with a dead layer on the SDD and potentially aluminum within the APXS. A silicon peak at 1.74 keV arises from interactions within the silicon detector. Titanium Kα and Kβ peaks (4.50 and 4.93 keV) are visible, sourced from the titanium foils covering the six sources and backscattered to the detector. The most prominent Ti peak in atmospheric spectra was observed after an IDD fault on sol 4116. The arm did not deploy the APXS to the intended rock target but still integrated in an off-nominal orientation. Imagery showed the IDD (constructed of Ti) at a distance faintly detectable to the APXS. Ti peaks are still present in nominal atmospheric spectra.

Chromium, nickel, and zinc (5.45, 7.48, 8.64 keV) Kα peaks are visible above the linear-dominated background. Chromium and nickel are sourced from stainless steel within the instrument, the origin of zinc is unknown. Gold Lα and Lβ peaks (9.71 and 11.49 keV) are attributed to the inside of the partially-closed APXS instrument doors and also the bonding used for the detector chips. Pb Lα and Lβ peaks (10.55 and 12.61 keV) are sourced from a plate behind the sources used for shielding.

There is a shelf-like feature at approximately 3.5-3.7 keV of unknown origin. Pu M lines from the 244Cm sources are generated in this energy region but do not possess the capacity to penetrate at a rate in excess of the Pu L lines. Furthermore, count rates should be lower than the titanium peak if these are backscattered Pu M lines. We also have no reason to believe this is a 3.69 keV Ca Kα peak. When fitting, the region is best fit with a 3.5 keV shelf, rather than a peak, possibly indicating some background associated with the argon signal. The argon K edge (Compton edge) was already included in the fit and sits at 3.2 keV. The shelf is also present in MER-A spectral sums.
### 3.4.3.2 Linear Background and Overflow Channel

The slowly varying linear background that spans the entire energy regime of a spectrum arises from incomplete energy dissipation (Compton effect) within the APXS SDD from high-energy events. High-energy photons from the neighboring Mössbauer instrument, cosmic background, and $^{238}$Pu within the rover’s radioisotope heating units (RHU) are all external sources of high-energy radiation affecting the background of the APXS. From the instrument itself, 0.02% of $^{244}$Cm decays create a 42.8 keV gamma ray. With a net source activity of $\sim$0.1-1 billion decays per second, there are potentially hundreds of thousands of gammas created by the APXS sources every second, each with the potential to interact with the detector and thus contribute to the background.

Detections with energy exceeding the upper limit of the spectrum are tabulated into the 512th channel (overflow channel). The correlation between linear background signal observed, and the count rate of events exceeding the upper energy limit of approximately 16 keV is strong ($R^2 = 0.92$), as expected.

### 3.4.4 Atmospheric Spectrum Count Rates

Count rates observed in APXS spectra are primarily dependent on sample-instrument separation. Atmospheric spectra are effectively obtained as separation increases to a point where the signal from the surface is negligible. However, the observed count rate of atmospheric spectra changes over time and is not entirely due to environmental changes. The six $^{244}$Cm APXS sources, with a half-life of 18.1 years [Bentley, 1968], provide excitation for the characteristic peaks as well as background signals. Both MER-A and MER-B are also equipped with a Mössbauer (MB) instrument. The Mössbauer is located beside the APXS on the end of the IDD and contributes to the APXS background due to its $\gamma$-emitting $^{57}$Co source with a half-life of 271 days [Klingelhöfer et al., 2003; Wdowiak et al., 2003].

Figure 3.3 illustrates the relative contribution from APXS and MB sources in MER-B atmospheric spectra. The fitted curves for the APXS (red, dashed) and MB (blue, dashed) have fixed decay rates and variable amplitudes. The data plotted are total count rates of channels 8 through 511. In atmospheric spectra, overflow channel counts contribute as much
as 70% of the total spectrum count rate. Inclusion of the overflow channel would hinder the observation of fainter signals. For this reason, it was excluded from the full spectrum sum. The total contribution (green, solid line) from APXS and MB sources nicely fits the observed APXS atmospheric full spectrum count rates. The MB has negligible contribution to APXS spectral count rates after approximately sol 1000 due to the decay of its $^{57}$Co source. Atmospheric data collected prior to sol 1000 are thus filtered out in the analyses that follow.

### 3.4.5 Zr Normalization

The Zr peak in atmospheric spectra is a suitable candidate for normalization due to its expected behavior in an infinite standoff environment. Normalizing the argon peak area to the zirconium peak area(s) compensates not only for the gradual decay of the APXS sources, but also for different measurement durations.

### 3.5 Analysis Methods

Multiple analysis models were tested to determine the reproducibility and uncertainty of each and thus the most suitable model for analyzing APXS atmospheric spectra. The models all contained a background component and determined peak areas through least-squares fitting or channel-specific sums. We removed data prior to sol 1000 and individual spectra within a given sol that had an average temperature warmer than -45°C. The reduced and energy-corrected data facilitated direct spectrum summation across all cycle times.

#### 3.5.1 Full-Spectrum Count Rates

The count rate variation of an entire spectrum (less the overflow channel) does illustrate consistency with anticipated atmospheric argon density. It is expected that the density of argon near the equator will cycle with a similar period to the annual pressure cycle due to the stability of the mixing ratio observed at the equator from orbit [Sprague et al. 2007; 2012]. Periodic oscillations follow the decay curve of the $^{244}$Cm APXS sources. Figure 3.4a illustrates the atmospheric full-spectrum count rate since sol 1000. Compensating for source
decay removes the downward trend without amplifying relative uncertainties, as plotted in Figure 3.4b. Scatter arises from variability in background count rates. Significant improvement can be achieved through analysis methods that include a background component.

3.5.2 Model Testing on High-Frequency MER-A Atmospheric Spectra

Daily atmospheric measurements with the MER-A APXS were commanded over the course of several weeks towards the end of the mission. The lack of rover motion combined with ample power to spare permitted these unique data to be collected. This month of high-frequency and long-duration atmospheric measurements provided the ideal data set to compare models and determine which was most appropriate to apply to the wealth of MER-B atmospheric spectra. These spectra contain over 189 hours of good-temperature data during a timeframe where there is little anticipated atmospheric pressure variability (Solar Longitude, $L_s$, 295 - 320). We use these consecutive high-frequency long-duration measurements by the Spirit rover as a verification campaign for the method and the analysis models applied due to the absence of any laboratory verification of the argon partial pressure and the unpredictable conditions on Mars. After filtering, 19 sol-summed MER-A spectra starting on sol 1952 and ending on sol 1994 were used to test the three different analysis models. For each model, normalization was conducted through Cm-decay correction and later by the zirconium peak.

3.5.2.1 Model 1: Specific Channel Range Count Rate

The first model involved a count rate analysis (CRA model) that estimated the background under the argon peaks using several channels immediately adjacent on either side. Figure 3.5a illustrates a schematic used for this method. The number of counts in all three regions, A, B1, and B2, were calculated. The average counts per channel of B1 and B2 combined was subtracted from the count rate of each channel in A. The resulting total for A, normalized by the integration duration, represented the argon count rate. The same method was applied to determine the zirconium peak count rate for potential normalization.
3.5.2.2 Model 2: Gaussian(s) over Linear Background

The second model was a least-squares peak fit by way of two Gaussian functions with a linear background (GLB model). Figure 3.5b illustrates this model for the argon K\text{\textalpha} and K\text{\textbeta} peaks. A similar fit was conducted on the Zr peaks for the purposes of normalization. Due to the close convolution of the two Zr K\text{\textalpha} peaks, a single Gaussian was suitable, resulting in smaller uncertainty in the peak area than fitting both K\text{\textalpha} peaks. Errors from the least-squares fit are 2\sigma. The argon K\text{\textalpha} and K\text{\textbeta} peaks were fit independently, however, the K\text{\textalpha} peak was solely used to represent the argon peak area as the uncertainty in the K\text{\textbeta} peak (typically \sim 25\% for single-sol integrations) was much larger than that of the K\text{\textalpha} peak (typically 2-3\%). The expected K\text{\textbeta}/K\text{\textalpha} ratio is well-defined and thus this was valid means of maintaining reduced errors.

3.5.2.3 Model 3: Full Spectrum Fit

A full spectrum fit was conducted on each atmospheric spectrum (FS model). Appropriate characteristic peaks and background signals were included. The same fit routine as Gellert et al. [2006] was used to calculate peak areas.

3.6 Discussion and Results

The results of the three models applied to the high-frequency, short-timescale MER-A atmospheric data are presented. The model best suited for analysis was applied to the several Mars years of MER-B atmospheric data. The data analyzed were all single-sol-summed spectra adjusted for temperature. Multiplying the output peak areas by temperature (in Kelvin) produces a result proportional to the partial pressure of argon (p_{Ar}). Energy correction is not needed for MER-A.

3.6.1 Comparison of Models using MER-A Data

The most suitable model was determined based on its stability and the relative uncertainty in the data points. Over short time scales, especially around Ls \sim 300, the atmosphere is stable which should be reflected in the model output. Table 3.1 captures the relative uncertainty
in the stability (intercept error, data point error) of each model and normalization method. Figure 3.6 illustrates the stability results for the CRA model with source-activity normalization. The two high data points are not correlated with any anomalous background signal and persist across all models and normalization methods. Dashed lines correspond to the $2\sigma$ uncertainty in the zero-slope linear fit (solid line).

The CRA model with source activity normalization produced smaller errors than Zr normalization or models that involved least-squares fitting. Normalizing by Zr increased uncertainty due to the inherent uncertainty in the Zr count rate or peak area. The poor statistics, even when using good-temperature, long-duration, sol-summed spectra, resulted in larger uncertainties in least-squares fitting analyses.

3.6.2 Daily Cycle and Ideal Gas Law

Measurements of argon in the Martian atmosphere with the APXS should follow the ideal gas law. That is

$$ T \propto P \cdot n^{-1} \quad (3.1) $$

where $P$ and $T$ are pressure and temperature respectively and $n$ is the density. MER-A atmospheric data collected after sol 1950 were summed by temperature. The argon peak area was calculated by the CRA model. Source activity normalization was not required due to the short timescale compared to the half-life of $^{244}\text{Cm}$. From Equation 3.1, plotting temperature ($T$) against inverse density ($n^{-1}$, analogous to inverse of APXS Ar peak area) should result in a linear response. As illustrated in Figure 3.7, there is a clear and strong ($R^2 = 0.95$) correlation between $T$ and $n^{-1}$ in addition to a near-zero intercept, as is expected. A quantitative value on partial pressure, from the slope, is not possible without knowing the density.

The APXS sensor head temperature is not an ideal representation of the temperature of the local atmosphere. Variability in temperature measurements acquired by the APXS are partly situational (positioning, exposure to light or heat). Previous geologic integrations have resulted in temperature readings that vary by upwards of $10^\circ\text{C}$ during similar times of
day within a week. While Sprit was stuck, the IDD was not moved during the acquisition of the APXS atmospheric data, minimizing the effects of APXS orientation on temperature. Substituting the bivariate weighted linear fit [York et al., 2004] plotted in Figure 3.7 as the expected ideal gas law response, vertical deviations from the line were within $\sim 5^\circ$C for all data points.

### 3.6.3 CRA Model Applied to MER-B Data

The MER-A atmospheric data set provided the high-frequency atmospheric measurements within a short timeframe necessary for model comparison. From this comparison, the source-activity normalized CRA model produced the smallest relative errors across all metrics considered. This method was applied to MER-B spectra acquired from sol 1000 through 4529 to investigate potential equatorial annual atmospheric argon variability. The filtered MER-B atmospheric spectra underwent gain correction and were scaled by temperature.

Plotted chronologically since sol 1200, Figure 3.8a shows the p$_{\text{Ar}}$ periodicity matching closely that of a Mars year (MY, 669 sols), as expected - data from MY 29 only are plotted in Figure 3.8b. The improved stability of Figure 3.8a compared to Figure 3.4b exemplifies the importance of focusing on energy-specific channels and considering variability in the background contribution within those channels.

#### 3.6.3.1 Comparison with Measurements from other Spacecraft: Evidence for an Argon-Enriched Front

Measurements of the Martian atmosphere from the surface date back to NASA Viking missions in the 1970s [Sharman, R. D. and J. A. Ryan, 1994; Ryan, J. A., and R. M. Henry, 1979] including attempts to measure argon by way of X-ray fluorescence [Clark et al., 1976]. Since Viking, Mars Pathfinder [Battersby, 1997], Phoenix [Davey et al., 2010], and Curiosity [Martínez et al., 2017; Haberle et al., 2014; Harri et al., 2014] have also added to this data set, including measurements of surface pressure. Both Viking missions and Curiosity have acquired pressure data over multiple Mars years. The Mars Exploration Rovers Spirit and Opportunity were not equipped with a conventional pressure monitoring instrument. Through regular measurements of the Martian atmosphere with the APXS
on these rovers, relative changes in argon partial pressure follow closely the atmospheric pressure changes observed by other missions in both relative variability and timing. This behavior is expected as the mixing ratio of argon in the equatorial atmosphere has been observed from orbit to be effectively constant to within the uncertainty (∼1% absolute) of the measurements [Sprague et al., 2007; 2012]. Modeling of the argon mixing ratio in the equatorial region of Mars does show variability over the yearly cycle [Forget et al., 2006; Lian et al., 2012]. Using the first 2-3 years of MER-B APXS atmospheric data, previous work by Arvidson et al. [2011] and Lian et al. [2012] captured variability in the argon mixing ratio with the change in seasons. However, a detailed description of the method is not provided and the data presented have larger uncertainties.

In Figure 3.9a, the relative pressure variability over the course of a Mars year is plotted for Viking 1, Viking 2, and the Mars Science Laboratory (MSL) rover Curiosity. The pressure is normalized to $L_s$ 0 (northern spring equinox) to minimize location effects and permit a more direct comparison with the argon data acquired by the MER-B APXS. Argon partial pressure data from the CRA model, plotted against $L_s$ and normalized to $L_s$ 0, are illustrated in Figure 3.9b, where the color corresponds to the labeled Mars year. The MSL normalized pressure curve is overlain as a dashed blue line and is assumed to be nearly equivalent to the relative pressure changes near MER-B - supported by global climate modeling [Forget et al., 1999; 2008]. A year-to-year comparison in Figure 3.9b shows consistency within the APXS data, especially during the transition period from low through high $p_{Ar}$ ($L_s$ 150 to 270). This supports the summation of spectra by $L_s$, further reducing uncertainties.

Figure 3.9c illustrates spectral summation by $L_s$, in 144 bins 2.5 $L_s$ in width, yielding improved statistics and reduced errors. Figure 3.9d focuses on the $L_s$ 90-270 transition from low to high pressure, with bins of equal width to Figure 3.9c - the inset captures the normalized pressure measured by Curiosity’s Rover Environmental Monitoring Station (REMS) instrument. A qualitative comparison of MER-B $p_{Ar}$ with Viking and Curiosity pressure shows agreement in both relative timing and magnitude of the variability (Figure 3.9c). The magnitude, from 90% to 110% of $L_s$ 0, agrees most closely with REMS measurements, likely due to the close proximity to the equator for both the MER-B (∼2°S latitude) and MSL (∼5°S latitude) spacecraft. The $p_{Ar}$ points in Figure 3.9c and Figure 3.9d centered at $L_s$ 154
and Ls 171 are anomalously low. These Ls bins represent a single sol of measurements only (sol 4377 and 3739 respectively). There is nothing specific about the rover location during the acquisition of the measurements. Careful inspection of the data found no root cause for the low argon peak areas. One possible explanation is a short-lived local weather event that is not buffered in the data by the benefit of multiple measurements within a single bin.

Measurements made by conventional pressure monitoring devices on the surface of Mars measure the CO₂-dominated pressure. The variability in abundance of argon in the atmosphere has a negligible (sub-percent) effect on these pressure measurements. The APXS measures the atomic abundance (density) of argon in the atmosphere, independent of the total atmospheric pressure and thus independent of the atomic abundance of CO₂. Argon accumulates at the poles, while CO₂ is freezing out of the atmosphere, resulting in significant local polar Ar enrichment [Sprague et al., 2004; 2007; 2012; Nelli et al. 2007; Feldman et al. 2003]. Near the equator, local pressure decreases at the onset of winter as the air mass moves to the winter pole, reducing the density of argon in the atmosphere. This explains the change in argon density and the overall pAr periodicity observed by the MER-B APXS matching closely that of the equatorial pressure cycle. Variations in the argon mixing ratio are measured from orbit, though not in the equatorial region. The sensitivity of the APXS to measure argon is higher than that of orbital measurements - a ~15% relative change in argon at the equator is not resolved from orbit.

The observed mixing ratio, taken as the ratio of the normalized p_{Ar} to the normalized REMS pressure curve (i.e. red dots divided by blue dashed line in Figure 3.9c), is presented in Figure 3.9e. The normalization of both p_{Ar} and MSL pressure to L_{s} 0 is not ideal. For comparison, the GCM-anticipated Ar mixing ratio curve from Forget et al. [1999; 2006; 2008], Lafèvre et al. [2009], and Lian et al. [2012], working from data presented in of Arvidson et al. [2011], note the noisiness and large errors in existing atmospheric APXS analyses. Through careful consideration of uncertainties and proper summation of data, the atmospheric APXS data in Figure 3.9 offer a significant
improvement over exiting work. Most notably, a new feature observed in the APXS argon measurements presented here was unresolved in previous work and not captured in modeling.

From Figure 3.9c, the lowest $p_{\text{Ar}}$ is observed by the APXS around $L_s$ 135 and increases rapidly to $L_s$ 150. The argon partial pressure then relaxes, leveling off or even decreasing slightly until $L_s$ 165, before increasing at a rate similar to the REMS pressure curve. This abrupt $p_{\text{Ar}}$ increase, presenting as a spike-like feature, is centered around $L_s$ 150 (emphasized in Figure 3.9d). The short-lived jump in argon density is statistically real across the various $L_s$ bin widths tested and persists from year to year (see Figure 3.9b). Faintly visible in Figure 3.9d but emphasized by the inset, the MSL spacecraft observed a slight (1% relative or $\sim$2x above reported uncertainty [Martínez et al., 2017]) bump in the observed daily average pressure, also centered at $L_s$ 150, right when the APXS measures a $\sim$-10% increase in $p_{\text{Ar}}$. This equatorial pressure bump measured by REMS could be the result of a sharp enrichment in argon. Assuming a $\sim$-5% total non-condensable gas abundance and a 10-15% relative increase in non-condensable gasses (including Ar and N2), a 0.5-0.75% change in the overall atmospheric pressure is expected. This magnitude is of the correct order of the pressure bump observed by REMS.

To explain the deviation from existing models and previous work where only a smooth change in mixing ratio is observed, we propose a front, enriched in argon, migrating away from the south pole, as the cause of the abrupt rise in measured argon abundance at $L_s$ 150. During the sublimation of CO$_2$ from the southern polar cap, a global pressure gradient drives the southern polar air mass northward from the CO$_2$ source at the south pole. As argon does not freeze out at the poles, the atmosphere at the south pole is up to 5x enriched in argon [Sprague et al., 2004; 2007; 2012; Lian et al., 2012] and ultimately constitutes the northward air mass. The front itself is enriched in argon with a level of enrichment that decreases during the migration as the front approaches the equator. Sprague et al. [2007; 2012] capture the seasonal variability in argon abundance with latitude from orbital measurements, supporting the northward argon-enriched front theory observed by the MER APXS. Forget et al. [1999; 2006; 2008], Lafèvre et al. [2009], and Lian et al. [2012] capture the variability in mixing ratio at the equator in their global models, but without the abrupt and short-lived argon enrichment around $L_s$ 150. A similar process occurs during northern winter at the north
pole but the effect is significantly reduced due to northern winter occurring near perihelion. There is a hint of a southern-moving front of enriched argon around $L_{\odot} 325$ ($\sim 180^\circ$ opposite the main $L_{\odot} 150$ observation) in the APXS data (Figure 3.9b-c), however, statistics are poor and thus currently inconclusive.

The variability in argon mixing ratio observed at Meridiani Planum by Opportunity is also supported by surface measurements on the opposite side of Mars. Trainer et al. [2017] through quadrupole mass spectrometer (QMS) measurements with the Sample Analysis at Mars (SAM) instrument on Curiosity show a similar increase in the argon mixing ratio shortly after $L_{\odot} 150$. The observed mixing ratio in Figure 3.9e consistent with Trainer et al. [2017] not only in the broadness of the enrichment but also relative enrichment magnitude and dilution. Limited mixing between the atmosphere above and inside Gale Crater, the MSL landing site, is predicted [Rafkin et al., 2016]. The pressure inside Gale Crater is not anticipated to be affected. However, short-timescale changes in argon, such as the frontal spike, may not be observable on the floor of the crater. Even so, the QMS and APXS data sets do complement each other nicely given the high-frequency of APXS measurements paralleling the low-frequency but high-accuracy SAM QMS results. With Curiosity and Opportunity on opposite sides of Mars, the observed change in argon mixing ratio observed by the MER-B APXS is not a local phenomenon.

The argon-enriched air mass over the southern polar cap migrates northward prior to the bulk transport of sublimated CO$_2$ that is responsible for the equatorial pressure increase. This results in the equatorial argon density (and $p_{AR}$) leading the primary pressure curve increase by $30^\circ$ $L_{\odot}$ (Figure 3.9c). The reduction in mixing ratio during southern autumn is a result of CO$_2$ sublimation from the northern seasonal cap [Lian et al., 2012]. With Curiosity perched south of the northern rim of Gale Crater, the local atmosphere is somewhat shielded from a southbound air mass, explaining why the MER-B APXS observes greater dilution during this time of year than is observed by SAM. The data in Figure 3.9 additionally show equatorial argon dilution during southern spring caused by sublimated CO$_2$ sourced from the southern polar cap during argon enrichment in the north polar region. Removing the $\sim 30^\circ$ $L_{\odot}$ shift, for illustrative purposes, the agreement between $p_{AR}$ and atmospheric pressure curve is apparent in Figure 3.9f.
3.7 Summary and Conclusions

After approximately six Mars years of observations, the MER-B APXS obtained over 1,600 hours of good-resolution atmospheric spectra. With this level of statistics, extremely low count rate signals were resolved once variability in temperature compensation was corrected. This permitted study of the ubiquitous APXS background to an unprecedented level of detail. The MER-A APXS offered high-frequency long-duration measurements over a short timeframe during a period of stable atmospheric pressure. The MER-A data facilitated testing of multiple models to determine the most suitable for analyzing atmospheric APXS spectra and capture variations in argon density with minimal uncertainty. These MER-A measurements also, when summed by temperature, confirmed ideal gas law behavior as a model consistency check.

Argon partial pressure variation was observed over several Mars years to match the expected mixing ratio predicted by current models and offers a significant reduction in uncertainty compared to previous work. Furthermore, for the first time, an annual short-lived equatorial enrichment (\(\sim 10\%\)) in argon was observed. Centered around \(L_s 150\), the spike in atmospheric argon is evidence of an argon-enriched front moving northward from the south pole during southern spring prior to the bulk transport of \(CO_2\). The enrichment in the front is smaller than the uncertainty of past orbital observations which focused primarily on the polar regions. The front was not detected by previous work reporting MER APXS atmospheric measurements. Another weaker front, originating from the north polar cap, could possibly be confirmed through more measurements focused around \(L_s 325\). Outside of the detected argon burst(s), the observed mixing ratio is in agreement with GCMs, atmospheric measurements with the MSL SAM QMS, and offers a significant statistical improvement over existing work.

3.8 Acknowledgments, Samples, and Data

The authors thank the dedicated team of engineers and scientists at NASA and JPL who made and continue to make the MER mission possible. The MER APXS was developed and built in the Department of Cosmochemistry in Mainz, mainly funded by the Max Planck
Society and, in part, by the German Space Agency (DLR). This work was lead by researchers supported by the Canadian Space Agency under contract 9F052-14-0592 for the MSL APXS. Clark and Ming are funded by NASA’s MER Participating Scientist Program. MER APXS, Viking and MSL/REMS data used in this study are available on the PDS. Processed MER APXS data products are available upon request. GCM data kindly provided by François Forget of Laboratoire de Météorologie Dynamique.

References


[60] - Forget, F., et al. (2006), Non-condensable gas enrichment and depletion in the martian polar regions, Second workshop on Mars atmosphere modelling and observations, Granada,
Spain.


3.9 Tables

Table 3.1: Three models and two normalization methods were tested on MER-A atmospheric spectra during a time period of high-frequency long-duration atmospheric measurements with the APXS. Due to poor statistics, uncertainties are higher when peak fitting algorithms are applied. To minimize uncertainties, absent issues in dead time, a count-rate-based analysis (CRA model) correcting for source activity provided the lowest uncertainty (<2% for data points). All models had approximately the same scatter in the data with the intercept-normalized standard deviation ranging from 0.03-0.04.

<table>
<thead>
<tr>
<th>Model Normalization</th>
<th>CRA SA</th>
<th>Zr</th>
<th>GLB SA</th>
<th>Zr</th>
<th>FS SA</th>
<th>Zr</th>
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<tr>
<td>Intercept Error (Rel. %)</td>
<td>1.57</td>
<td>1.88</td>
<td>1.64</td>
<td>2.01</td>
<td>1.72</td>
<td>2.01</td>
</tr>
<tr>
<td>Mean Data Error (Rel. %)</td>
<td>1.90</td>
<td>2.59</td>
<td>2.03</td>
<td>3.89</td>
<td>3.15</td>
<td>4.54</td>
</tr>
</tbody>
</table>

3.10 Figures

Figure 3.1: (a) Comparison of a MER-B APXS geologic spectrum (blue, target = Tennessee RAT, sol 139, $T_{av} = -64^\circ C$, duration = 11h39) and an atmospheric spectrum (red, sol 79, $T_{av} = -60^\circ C$, duration = 15h56). (b) Least-squares fit (black, bold line) of a filtered and energy-corrected sum of 1614.5 hours of MER-B atmospheric spectra (data in grey). Red lines correspond to elemental peak curves, blue lines correspond to Cm-sourced scattered Pu L lines (Compton and Rayleigh peaks). Green lines correspond to linear and bremsstrahlung backgrounds.
Figure 3.2: Gain (a) and offset (b) of MER-B atmospheric samples. Each peak position was determined by a model consisting of Gaussian and linear background functions applied to the Ar and Zr peaks. For gain, data points are color coded corresponding to sequence cycle time. Offset is typically within one channel of 0 eV. (c) Uncorrected energy compensation illustrating peak shift between “short” and “long” cycle time with the Ar K$_\alpha$ and K$_\beta$ emphasized below. (d) Corrected energy compensation illustrating peak alignment for direct summation independent of cycle time.
Figure 3.3: MER-B APXS atmospheric X-ray spectrum count rate (channels 8 to 511). Green curve corresponds to a fitted sum of $^{57}$Co (blue) and $^{244}$Cm (red) decay curves. Oscillations about the green curve are the result of seasonal changes in atmospheric (argon) density. The contribution from MB to APXS count rates is negligible after sol 1000.

Figure 3.4: (a) Raw single-sol sum full spectrum count rates. Overflow channel not included in the sum. (b) Normalized by source activity at sol 1.
Figure 3.5: (a) Specific channel range count rate method (CRA model) for the argon K\textsubscript{\textalpha} and K\textsubscript{\textbeta} peak region of an atmospheric spectrum. The average count rate of regions B1 and B2 combined was subtracted from the count rate of each channel in A to give an estimate for the argon peak area. (b) Gaussian curves with a linear background for the argon K\textsubscript{\textalpha} and K\textsubscript{\textbeta} peak region of an atmospheric spectrum (GLB model) to determine the argon peak area. Data plotted in both figures are a sum spectrum of all filtered MER-B energy-corrected spectra.

Figure 3.6: Temperature-adjusted MER-A argon count rate (partial pressure) from sol 1952 to 1994 during a time of anticipated stable atmospheric argon density. Dashed lines correspond to 2\sigma uncertainty in the zero-slope linear fit (solid line). The model and normalization method that minimizes the error in the data points and results in the most stable fit is best suited for the analysis of MER-B data. Data plotted here are from the CRA model normalized by source-activity.
Figure 3.7: MER-A spectra summed by temperature. No normalization was necessary due to the short sol range. $R^2 = 0.95$. 

Figure 3.8: a: Temperature-adjusted CRA model with source activity normalization since sol 1200. b: Results from MY 29 only (sols 1381-2041) plotted by solar longitude ($L_s$).
Figure 3.9: (a) Viking and MSL pressure data normalized to $L_s$ 0. (b) MER-B argon partial pressure ($p_{Ar}$, source-normalized and temperature-adjusted argon count rate) from the CRA model. Data from MY 28-33 plotted and normalized to $L_s$ 0. (c) Atmospheric spectra binned into 144 $L_s$ bins and summed for improved statistics. (d) Focus on $L_s$ 90-270 emphasizing the rapid increase in $p_{Ar}$ observed from $L_s$ 135-165 before an increase is maintained that parallels the pressure gradient observed by MSL. Blue dashed line in b-d corresponds to MSL MY 32 normalized pressure data. (e) Ratio of normalized MER-B $p_{Ar}$ to normalized MSL-measured pressure illustrating the changes in mixing ratio observed with the MER-B APXS. Abrupt enrichment is observed at $L_s$ 150. GCM anticipated Ar mixing ratio curve from Forget et al. [1999; 2008] and resulting residual also displayed. Linear interpolation in residual values applied where $L_s$ bins were absent APXS measurements. (f) APXS $p_{Ar}$ shifted 30 $L_s$ to illustrate agreement in relative timing and amplitude with the MSL pressure curve.
Chapter 4

Unpublished Work

The work presented in this chapter was relevant for previous publications, presented in §2 and §3, has been presented at conferences, and/or is planned for future publication. In the case of the latter, specifics that would permit direct replication are omitted.

4.1 Layer Modelling

Usual APXS calibration and analysis assumes an infinitely thick sample. The penetration of X-rays and alpha particles into the sample, the excitation of X-rays over depth, and the probabilities for the X-rays to exit the sample is convoluted into the yields of each element. A simple layer model can be constructed, modelling the signal for each element as a sum of integrals over each layer. We assume negligible secondary (matrix) effects as the uncertainties within the modelling, specifically the uncertainties in layer thickness, are in excess of errors resulting from neglecting matrix effects. The X-rays modelled are the characteristic X-rays, after excitation by the incident Pu L X-rays and alpha particles from the APXS, and the varying attenuation based on sample composition and depth.

For the simplest example, a two-layer system, the top layer, $L_T$, has thickness $T$ and the bottom layer, $L_B$, is infinitely thick. The linear attenuation coefficient, $\lambda$, gives relative intensity of X-rays originating from within the top layer of thickness $T$ as

$$L_T = \int_0^T \exp(-\lambda x) \, dx = \frac{(1 - \exp(-\lambda T))}{\lambda} \to (1 - \exp(-\lambda T))$$  \hspace{1cm} (4.1)
where the X-rays originating from the bottom layer are given by

$$L_B = \int_T^{\infty} \exp(-\lambda x) \, dx = \frac{(1 + \exp(-\lambda T))}{\lambda} \rightarrow (1 + \exp(-\lambda T)).$$  \hspace{1cm} (4.2)

The $\lambda$ in the denominator is dropped as it cancels out later in the sequence. Provided two of layer thickness, $T$, upper layer concentrations, $U$, and bottom layer concentrations, $B$, are known or assumed, a least-squares analysis is used to solve the system in Equation 4.3, minimizing $\left( \frac{M-C}{\Delta C} \right)^2$ where $M$ is the least squares modelled concentrations, $C$ is the target or measured concentrations with errors $dC$.

$$M_i = 100 \cdot \frac{(1 - \exp(-\lambda T_i \cdot T)) \cdot U_i + \exp(-\lambda B_i \cdot T) \cdot B_i}{\Sigma_i (1 - \exp(-\lambda T_i \cdot T)) \cdot U_i + \exp(-\lambda B_i \cdot T) \cdot B_i}$$  \hspace{1cm} (4.3)

The linear attenuation coefficients (units length$^{-1}$) for known or assumed compositions are derived from an assumed homogeneous mixture of the atoms in the appropriate abundances. For calculated layer compositions, the linear attenuation coefficients are estimated based on an average Mars composition. This is a reasonable initial approximation and can be refined after each iteration when the least-squares system is solved, if so desired. Furthermore, density can be defined for each layer, beneficial when modelling layers of significantly different densities (e.g. Mars dust atop an igneous composition).

### 4.1.1 Layering on the High-Mn Target Stephen

If, for example, only the bottom layer concentrations are known or assumed, the system can still be solved, but only iteratively for a given assumed thickness of the top layer. This was conducted using the APXS composition obtained on a small rock, named Stephen, with a thin low-albedo surface fracture fill [21, 44]. One possible explanation for the unique chemistry of Stephen, in comparison to the surrounding area, is a thin layer of a unique composition overlying the typical bedrock composition of that area.

The dust-free endmember from [21] was used as the target composition, $C$. Windjana from [40] was assumed as the lower-layer composition, $B$. The top-layer composition, $U$, was derived for a series of thicknesses. Density was assumed to be $3.0 \text{ g} \cdot \text{cm}^{-3}$ for both the
upper and bottom layer. The results are presented in Table 4.1.

As a consistency check, as the thickness of the top layer becomes optically thick, the top layer model composition, $U$, approaches $C$, the “observed” values. For the very thin (1 or 2 μm) layers, there are extreme enrichments in the modelled top layer in an attempt to better fit the observed composition. However, this is accompanied by a rather large $\chi^2$. The goodness of fit of the model, judged by the $\chi^2$, quickly flattens off around $T=5-10$ μm. A layer 5-10 μm thick is completely plausible for this target and the results generated by the model in this thickness range are reasonable. Specifically, 10-20 wt% MnO in a 5-10 μm thick layer atop Windjana (0.5 wt% MnO) results in a measured MnO concentration very close to the measured (or deconvolved) value (4.4 wt%). The measured concentration of trace elements (Ni,Zn,Br) are all 2-5x higher in the observed than in the assumed bottom layer. This results in exceptionally high values in the 5-10 μm top layer (0.4-0.7 wt% Ni, 2.5-4.2 wt% Zn, 1.4-2.8 wt% Br) due to the bottom-layer-dominated source region of X-rays of higher energy. However, careful examination of the CCAM data shows only a slight depth dependence of MnO, effectively ruling out a few-μm thick top layer. A more-likely thickness would be on the order of 10-50 μm, supported by the results presented in Table 4.1. A 10-50 μm-thick layer would require 5-10 wt% MnO to give an observed concentration of 4.4 wt% MnO given 0.5 wt% in the lower layer (Windjana). The uncertainty in thickness results in the ±5 wt% MnO uncertainty, central to the layer modelling dilemma with APXS data on Mars where limited information is available. The layer model algorithm presented here is planned for future injection into the APXS deconvolution routine to better handle the interplay of dust-covered and dust-free surfaces. It is also being considered for future submission to a relevant journal.

4.2 Simulations

Several simulation algorithms have been generated for the improved study and understanding of the APXS method. This section will focus on two simulation algorithms of the most significant interest.
Table 4.1: A layer with unique chemistry modelled on top of Windjana (Bottom) to form the dust-free Stephen endmember (Measured) from [21]. The range of top layer thicknesses illustrates the different modelled chemistry of the top layer depending on its thickness. The table is most easily read as the top layer of certain thickness over “Bottom” yields closely “Measured”. Concentrations are in wt% unless otherwise stated. Errors correspond to the range in top layer chemistry that increases the $\chi^2$ by 1.

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<tr>
<th>Top (μm)</th>
<th>Na$_2$O</th>
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<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>P$_2$O$_5$</th>
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<th>CaO</th>
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<td>0.73±0.10</td>
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<td>3.30±0.35</td>
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Bottom 0.39±0.12 12.78±0.09 5.71±0.02 39.58±0.28 0.73±0.01 2.64±0.07 0.79±0.07 3.66±0.07 4.90±0.09

Measured 1.01±0.1 18.35±1.84 4.18±0.42 33.50±3.35 0.73±0.07 4.43±0.44 3.30±0.33 2.43±0.24 4.17±0.42

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<th>TiO$_2$</th>
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<th>MnO</th>
<th>FeO</th>
<th>Ni (μg/g)</th>
<th>Zn (μg/g)</th>
<th>Br (μg/g)</th>
<th>$\chi^2$</th>
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<td>8347±845</td>
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<td>3.94E-07</td>
</tr>
</tbody>
</table>

Bottom 1.18±0.03 0.42±0.03 0.52±0.04 26.18±0.47 378±69 4316±389 419±71

Measured 0.86±0.09 0.34±0.03 4.42±0.44 21.12±2.11 1362±136 8347±835 1917±192
4.2.1 APXS Instrument Response

Pertinent to the work presented in §2.1 and §2.2 is an understanding of the sensitivity of the APXS. This section will present work conducted to better understand the off-nadir (lateral or radial) sensitivity. A thorough enough description of the vertical sensitivity of the APXS can be found in §2.2, specifically presented in Figure 2.13.

A Monte Carlo approach was applied to approximate the radial sensitivity curve for the APXS. All parameters including standoff and collimator dimensions are free to the user's choosing. In the interest in computational efficiency, the isotropic emission is calculated from one source and replicated into the appropriate reference frame for each of the other five sources. The location of contact between emitted event and the surface is tabulated into a NxN grid of pre-defined width. Logging events into a grid is more computationally efficient than logging each individual event. Adding another count to a cell within a grid as opposed to appending coordinates to an ever-growing list of surface interaction locations significantly improves efficiency, especially as the number of computed emissions exceeds $10^5$. Once a pre-defined number of iterations has concluded, the return trajectories are simulated through geometric weighting.

Simulating the return trajectory of each created characteristic X-ray back to the detector would result in considerable computational time waste as the majority will go undetected. Instead, the values in each cell are scaled by the relative surface area of the collimator that is visible. Scaling by the relative visible detector area is computationally fast and an accurate enough representation of the solid angle visible to the isotropic emission of the characteristic X-rays excited from within the sample from each cell within the NxN grid. The separation between the collimator window and the sample surface ($h$), the length of the collimator ($h_c$), and the collimator radius ($r_c$) all govern the detector area visible to each cell within the grid.

The solution contains two scenarios. The first occurs when the characteristic X-ray is emitted from an area directly below the collimator opening. The second, and more common, scenario is a characteristic X-ray emitted from the surface for an area whereby the collimator opening is not directly zenith. The two scenarios are outlined in Figure 4.1 (not to scale) where the red arrow illustrates the relative viewable opening in one dimension. Applying
this method for both lateral offsets from detector nadir gives a relative two-dimensional area in the form of an ellipse by which the total counts in each N×N cell are scaled.

Figure 4.1: Model for simulating detections of characteristic X-rays from the sample surface. Relative visible dimension outlined in red. When used for both vertical and horizontal offset from detector centreline, the result is a relative surface area for each position interrogated by the APXS instrument. Figure is not to scale.

The linear dimension, when lateral displacement is \( < r_c \) from detector centreline is given by:

\[
x = 2r_c \left( 1 - \frac{h_c}{h + h_c} \right).
\]  
(4.4)

For lateral displacement \( > r_c \), the linear dimension is given by:

\[
x = 2r_c - h_c \left( \frac{r_c \pm x}{h + h_c} \right).
\]  
(4.5)

Logically, as the aspect ratio of the collimator becomes higher and in favour of \( h_c \), the visible dimension decreases. Also, for \( x < r_c \), the visible dimension is independent of \( x \). The \( r_c \pm x \) in Equation 4.5 is necessary to handle negative \( x \) values and ensure a non-negative
visible dimension. The same process is repeated for the \( y \) dimension to achieve two visible dimensions for each cell. The visible area is then given by:

\[
A = \frac{\pi}{4}xy
\]  

which is the area of an ellipse and is a close approximation to the detector solid angle visible for a given point on the surface.

Simulation time is under 60 seconds for \( 10^6 \) iterations. There is very good agreement with the MER APXS lateral sensitivity curve, derived during laboratory testing, when parameters are set as \( r_c = 1.5 \text{ mm} \) and \( h_c = 8.75 \text{ mm} \) - both on the order of what would be expected for the collimator in use by the MSL APXS. The actual dimensions are not conclusively known. The value for \( h \) is variable depending on the intended instrument standoff, however, 18.0 mm is defined as “contact” with the surface by the contact sensor. Plots of the APXS lateral sensitivity are not included for proprietary purposes.

### 4.2.2 Empirical APXS Full-Spectrum Simulation

Simulated APXS spectra can be used to probe how certain aspects of integrations affect results. Simulating every step of the process from emission, through target interaction, and detection, is incredibly tedious to do with any level of accuracy. Here, an empirical approach is applied whereby many APXS spectra are fit and the various parameters are observed against variables like temperature and standoff. A spectrum can then be reverse engineered allowing the official fit software to be probed to see the response in situations that are not commonly observed on Mars. Furthermore, development of a least-squares fit routine was immediately applicable to the work presented in §3.

When fitting an APXS spectrum, there are three primary components:

1. background lines

2. characteristic peaks, and

3. scatter peaks.
4.2.2.1 Background Lines

The background lines are most easily visible in atmospheric spectra, like those presented in §3. There is a slowly varying linear background that spans the entire energy regime of the spectrum. This linear background (see Equation 4.7) is a result of interactions between high-energy photons and the APXS detector whereby only part of the high-energy photon’s energy is dissipated by the silicon crystal. There is also a background signal that dominates the low-energy end of a spectrum, of bremsstrahlung source, most easily visible in atmospheric spectra. The bremsstrahlung background is modelled by Equation 4.8 based on the work of [28].

\[
\begin{align*}
B_1 &= m \cdot E + b \\
B_2 &= P_1 \cdot \exp \left( -\frac{(E + P_2)^2}{2 \cdot P_3^2} \right) + P_4 \cdot E \cdot \exp \left( -\frac{E^2}{2 \cdot P_5} \right)
\end{align*}
\] (4.7) (4.8)

Parasitic peaks are also considered background, most notably coming from the instrument (e.g. Zr from the collimator) and the surrounding environment (e.g. atmospheric Ar). Fitting of these background signals follows §4.2.2.2 due to the nature of the lines.

4.2.2.2 Characteristic Peaks

The structure of characteristic peaks is a convolution of several structures resulting from interactions between the detected photon and the detector. There is the primary peak, \( G \), following a Gaussian distribution due to the statistical variability in charge collection within the APXS SDD. Incomplete charge collection is modelled by two exponential tail functions, \( T_1 \) and \( T_2 \). Escape peaks, resulting from Si K\( \alpha \) X-rays escaping the active area of the SDD during interaction, are modelled by \( X \). The Compton edge, a shelf-like structure also arising from incomplete charge collection, is modelled by \( S \). The total line for a single peak is by \( L \), the hypermet function. That is,

\[
L = G + T_1 + T_2 + X + S.
\] (4.9)
The specific equations for each structure that results from the detector response to interacting photons are given by

\[ G = \text{scale} \cdot \frac{A}{\sqrt{2\pi}\sigma^2} \exp\left(-\frac{(x - \mu)^2}{2\sigma^2}\right) \]  
(4.10)

\[ T_1 = \text{scale} \cdot \exp\left(\text{TSF}_A + \text{TSF}_B \cdot E\right) \cdot H \cdot \exp\left(\frac{x - \mu}{\sigma \cdot \text{TSF}_C}\right) \cdot \text{erfc}\left(\frac{x - \mu}{\sqrt{2\sigma}}\right) \]  
(4.11)

\[ T_2 = \frac{1}{\sqrt{2 \cdot \text{TSF}_C}} \]  
(4.12)

\[ X = \begin{cases} 
\text{scale} \cdot H_{\text{esc}} \cdot H \cdot \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right), & \text{if } E \geq E_{\text{esc}} + 400 \text{ eV} \\
0, & \text{otherwise}
\end{cases} \]  
(4.13)

\[ S = \exp\left(S_A + S_B \cdot E\right) + H \cdot \left(1 - \text{erf}\left(\frac{x - \mu}{\sqrt{2\sigma}}\right)\right) \]  
(4.14)

where

\[ \mu = \frac{E - \text{Offset}}{\text{Gain}}, \text{ and} \]  
(4.15)

\[ \sigma = \frac{\sqrt{\text{FF} \cdot E + \text{FWHM}_0}}{2.355 \cdot \text{Gain}}. \]  
(4.16)

\( E \) is the energy of the characteristic line, \( A \) is the area and \( H \) is the height of the peak. For the main lines, \( \text{scale} = 1 \). For secondary lines, \( 0 \leq \text{scale} < 1 \). For K\( \beta \) peaks, \( \text{scale} = \frac{K_\beta}{K_\alpha} \).

### 4.2.2.3 Scatter Peaks

Scatter peaks are the result of both coherent and incoherent scattered photons sourced from the APXS instrument itself. These primarily manifest in APXS spectra as Gaussian peaks in the 11-22 keV energy range of the spectrum, sourced from Pu L lines. However, they do not follow the same FWHM behaviour nor peak form as characteristic peaks. Scattered Pu M lines are not obvious in APXS spectra due to their low intensity. Scatter peaks are modelled by

\[ \text{CR} = H_S \cdot \exp\left(-\frac{(x - E)^2}{2\sigma_S^2}\right) \]  
(4.17)

(4.18)
where $H_S$ is the height of the peak centred at energy $E$ with a FWHM of $2\sqrt{2\ln2}\cdot\sigma_S$. Coherent scatter peaks are more resolved than incoherent scatter peaks, with a FWHM that scales with $E$ - incoherent peaks are much broader.

### 4.2.2.4 Full Spectrum Fit

A spectrum is fit using

$$F = B_1 + B_2 + \sum_i L_i + \sum_j CR_j$$  \hspace{1cm} (4.19)

with the $i$ elements and $j$ scatter peaks defined by the user. The fit is conducted on a spectrum where channels are expressed in counts per second, maintaining consistency in initial conditions for the integration-time-sensitive variables. As a result, the weight associated with each channel in the fit is given by

$$W_i = \frac{1}{\sqrt{N_i}}$$

where $N_i$ is the total counts in channel $i$.

The actual fitting of the spectrum is executed using MATLAB’s built-in `fit` function exploiting the fully customizable equation and options settings. Due to permitting user customization of elements to be fit, the equation and options delivered to the `fit` function are constructed with each execution of the script. This results in a more powerful and versatile program, but significantly increased development time. Upon fit completion, the results are output along with $2\sigma$ uncertainty and various goodness of fit values. Plotting the spectrum, the resulting fit, and all the individual lines is at the discretion of the user. In addition to illustrating the impact of temperature on resolution (via FWHM0), the natural degradation in resolution over time as well as the Peltier cooler “FWHM bump” around $-50^\circ C$ is visible through preliminary fitting.

To simulate a spectrum, the spectrum is first built from the desired parameters before being converted into a cumulative distribution function (CDF). A uniform random number generator is applied and through the CDF curve a channel is selected for a count. Early
demonstrations have illustrated promising results. Figure 4.2 illustrates the significant improvement in the signal to noise ratio for trace elements when comparing a 10 minute integration to a 10 hour integration.

![Simulated spectrum of APXS target “Portage” after 10 minutes (left, red) and 10 hours (right, green). Temperature and standoff unchanged from actual Mars measurement.](image)

Figure 4.2: Simulated spectrum of APXS target “Portage” after 10 minutes (left, red) and 10 hours (right, green). Temperature and standoff unchanged from actual Mars measurement.

The impact of standoff is also readily output from early iterations of the simulation algorithm. Figure 4.3 illustrates the effect of increasing standoff from contact through 2 cm to 5 cm. While the increase in Ar peak (around channel 100) is obvious, the increased attenuation of low-energy signals like Na is not yet implemented. Count rate decreases sharply with increasing standoff (see Figure 2.13) and is especially problematic for trace elements further exacerbated by short integration times as illustrated in Figure 4.2.

Integration time and standoff are two parameters that are often within the control of the APXS operations team to manage and optimize in order to achieve peak measurement quality. It is possible to integrate during colder temperatures, however, that can only be selected for through careful timing of the integration. Integration timing may have restrictions due to the logistics of the rover’s plan for that sol. Furthermore, the composition of the target is unknown. Figure 4.4 illustrates the effect concentration variability and temperature have on a spectrum. In the left frame, the concentration of sodium is increased from 1 through 5 wt%; the peak area change clearly visible. In the case of the 2 cm standoff and -30°C simulated here, the signal to background for Na is approximately N:1 where N is
Figure 4.3: Simulated spectra of the APXS target “Portage” at contact (green), 2 cm stand-off (yellow), and 5 cm standoff (red). Increase in Ar peak (around channel 100) visible with increasing standoff. Increased attenuation of Na due to a longer air column not yet implemented. Temperature -50°C, integration time 1 hour.

the Na$_2$O concentration in wt%. In the right frame, the impact of temperature on resolution is displayed. The Na peak becomes significantly degraded with increasing temperature. Most peaks are not resolved above -5°C. The P$_2$O$_5$ peak around channel 63 is especially susceptible to warm temperatures due to its proximity to the spectrum-dominating silicon peak.

The program has undergone heavy development but is currently not in a state to be used to its full intended capacity. Atmospheric spectra have fewer lines than a solid-sample spectrum. The program fit and behaved as intended for the purposes of a full-spectrum fit model discussed in §3. With solid samples, more work is needed to improve the output of the fit routine. In its current state, the algorithm clearly illustrates its core functionality. The ability to test the response of official APXS fitting software on simulated spectra is incredibly powerful. The temperature at a given standoff where sodium becomes unresolvable or how
Figure 4.4: Left: Simulated spectra of the APXS target “Portage” with various Na$_2$O concentrations at -30°C and 2 cm standoff. Sodium concentrations plotted include (in wt%) 1.0 (purple), 2.0 (blue), 3.0 (green), 4.0 (yellow), and 5.0 (red). Na signal to background under these parameters scales approximately as N:1 where N is the concentration of Na$_2$O in wt%. Right: Simulated spectra of the APXS target “Portage” at various temperatures and 2 cm standoff. Na concentration set to 3.0 wt%. Temperatures plotted include (in °C) -50 (purple), -30 (blue), -10 (light blue), -5 (blue-green), 0 (green), 5 (yellow), and 10 (red).

long of integration is required at a given standoff to achieve a certain signal to background ratio for a specific element are just a few examples of how the script can be used in its completed form. One primary goal of the investigation is to verify the uncertainties and detection limits for samples with a low abundance of trace elements and their dependence on integration time, standoff, and composition at ideal temperatures.

4.3 Compositional Fitting with Known or Assumed Endmembers

The least-squares minimization routine utilized in §2 solves for the unknown composition of a known abundance of endmembers. This non-invertible matrix system can be re-arranged to solve for the unknown abundance of known endmembers. This can be applied when the FOV contains clearly a mixture of known compositions such as pebbles and soil mixed in the FOV.
4.3.1 Fixed Endmembers

When endmembers are fixed, each APXS target is investigated individually using endmembers pre-defined by the user. Careful consideration should be made to keep the endmembers as orthogonal as possible and not simply use an endmember list so extensive the results are of low confidence.

All MER-B APXS data were run using a limited number of endmembers. Common expected endmembers of average Mars (soil), Burns formation, magnesium sulphate, calcium sulphate, and iron oxide were input for the endmembers. In this case, a high \( \chi^2 \) is indicative of targets that are unique and do not fit well as a mix of common endmembers. Such targets include: Esperance, Bounce Rock, Marquette, San Torini, Lihir, Jean-Baptiste Charbonneau, Stuart Island, and so on. These targets are all of unique composition, and cannot be fit well with the common endmembers listed. One can also plot the abundance of Burns formation endmember vs. sol (proxy for traverse), and see roughly how the traverse of MER-B has ventured off and on Burns formation.

4.3.2 Iterative Process: Variable Endmember

As described in §4.3.1, APXS measurements can be fit using a least-squares technique of fixed user-defined endmembers. This method can be expanded, allowing for a variable endmember to be sought during the least-squares fitting. Due to the nature of the algorithm, by including a variable endmember, the process becomes iterative in nature. The initial conditions are randomized with each iteration but centre on the mean composition of the APXS measurements that are the goal of the fit routine. The variable composition is then adjusted until the lowest \( \chi^2 \) across the entire target list is achieved. The process is repeated and the best fit used as the final result. Errors are representative of the range in the variable endmember composition observed across the lowest 5% of results.

4.3.2.1 Application to Murray Formation APXS Data

The iterative endmember method was applied to better understand the Murray formation in Gale Crater as investigated by Curiosity and studied thoroughly with the MSL APXS.
Compared to average Mars, the Murray formation is distinctly characterized by low MgO and CaO concentrations accompanied by enrichments in SiO$_2$, K$_2$O, Zn, and Ge, with an elevated Fe/Mn ratio. While APXS analyzes show this pattern is consistent over kilometres, chemical heterogeneities arise from intermixed dust, sulphates etc. in the APXS FOV. Endmembers of thin dust, MgSO$_4$, CaSO$_4$ were selected to accompany a variable endmember composition. The thin dust endmember was calculated as the signal observed by the APXS from a 5 $\mu$m thick layer of Mars dust (composition from [30]) using the layer model presented in §4.1. The goal was to determine the composition of the Murray formation, absent measured variability caused by typical intermixed heterogeneities.

Figure 4.5 illustrates the derived composition for typical Murray (black, bold line) ratioed to average Mars. Noticeable differences are apparent when comparing to the direct Murray average (red dashed line). This captures the importance of considering the significant variation and subtle heterogeneities within the Murray formation when determining a characteristic composition. The range in compositions observed within the Murray formation scatters considerably around average Mars. However, as evident, the signature of typical Murray (black, bold) is distinctly characterized by the low MgO and CaO concentrations compared to average Mars. In addition, considering Ca-, Mg-sulphates and the potential contamination of a thin dust layer, typical Murray is significantly depleted in sulphur. The significant enrichments in K$_2$O, Zn, and Ge, compared to average Mars, are also evident in the derived typical Murray composition. These enrichments are not as clear when looking at the overall range of concentrations across all Murray targets (shaded grey background). The reader should note, the ratio of Ge is to the APXS limit of detection (LOD) for Ge since average Mars Ge is at or below LOD. Furthermore, Ca-sulphate is likely over-stripped from the derived composition. This is not a concern for results downstream as this is rectified by a simple addition of Ca-sulphate in the results that follow.

Figure 4.6 illustrates the ratio of measured to modelled concentrations of each target by sol. A ratio greater than unity indicates the measured concentration was higher on Mars than can be modelled by simply mixing dust, sulphates, and the previously derived typical Murray. This “enrichment” is interpreted as something extra that exists within the
Figure 4.5: Derived composition of the Murray formation (black, bold line) absent heterogeneities in the form of sulphates and dust. Red dashed line corresponds to the direct average of all APXS Murray targets (bounded by grey background). Ge is expressed as a ratio to APXS Ge limit of detection due to the low abundance of Ge in average Mars.

measured sample to give the increased concentration that the model cannot achieve. These enrichments in some instances may be too subtle to observe over the compositional noise caused by heterogeneities in the targets to varying extents. The most notable example of enrichment is Buckskin, one of the high SiO$_2$ samples, interrogated from sol 1057-1091. The model is not only unable to produce the high-SiO$_2$ composition as a simple mixing, but also other elements, like K, Al, and Ti, deviate significantly, indicating a significant compositional change from typical Murray [75]. Other examples of such systematic deviations are: the elevated Ni (and MgSO$_4$) of Morrison (sol 775, see §2.1 and §2.2), the elevated Al$_2$O$_3$ of Mojave (sol 800-900), and the gradually increasing Fe/Mn ratio (by decreasing Mn with near-constant FeO). One also sees the constant CaO, after the impact of CaSO$_4$ is removed, as well as the steady SiO$_2$, TiO$_2$, and FeO, aside from Buckskin. There also appears to be a downward trend in Mn and Zn along the traverse while there is an increase in Cl and Br (Br not plotted in Figure 4.6).

The encountered chemical homogeneity of the Murray formation, while a significant finding by itself with major implications for the geologic record at Gale, provides an opportunity to test these algorithms. The derivation of typical Murray composition, absent
Figure 4.6: Fit APXS compositions of the Murray formation using the derived typical Murray composition (see Figure 4.5), thin dust, CaSO$_4$ and MgSO$_4$ as endmembers. A ratio greater than one implies the model cannot construct the composition with the endmembers available and something unique to the target is enriched locally.

apparent CaSO$_4$, MgSO$_4$, and dust, is important as it permits the potential to detect and quantify faint variations within the Murray formation as Curiosity continues its traverse.

The reader should note, the model presented here is not sensitive to whether the sulphates are in veins, nodules, or cements. Sulphates within the bulk rock (detrital or cements) have
been observed in the Murray formation. Recently these sulphates are potentially subtracted in the deconvolution and have significant geological implications.

4.4 Automated Cluster Analysis: MER-B

Since 2004, MER-B has acquired over 440 unique APXS measurements, on a wide variety of compositions, during its 43+ kilometre traverse across different geological terranes. An analytical comparison algorithm was developed, providing a means to cluster samples based on compositional similarity providing an automated classification scheme.

Due to the inherent variance of elements in rocks and soils, each element has an associated weight that is inversely proportional to its variance. Elements whose abundances do not fluctuate much, such as SiO$_2$, are thus weighted more, and an atypically large deviation from what is commonly observed becomes a more defining characteristic for that target. Elements that naturally fluctuate widely, for example Br, then have a lesser influence on defining rock and soil classes. All elements standard to the APXS data set are considered. Measurement errors are used to weight the data - larger uncertainties reduce the weighting of the element. The comparison of two targets, $i$ and $j$, generates a similarity score, $S_{ij}$.

The algorithm facilitates the initial classification of APXS targets by chemistry alone, independent of target appearance and geological context which can be added later as a consistency check during final lithological assignment. For the $N$ targets considered, a $N \times N$ hollow matrix, $S$, is generated and equal to its transpose. The average relation score, $S_{av}$, for target $N_i$ is the average of column $i$ of $S$. A large $S_{av}$ is indicative of a unique sample. Targets with a low comparison score can be classified as being alike. While the current method of data clustering is effective, improvements or an alternative means are necessary due to a slight nearest-neighbour bias in the clustering method presented in Table 4.2 and Figure 4.9.

4.4.1 Automated Cluster Analysis Results

The cluster analysis algorithm, using strictly chemical compositions, successfully grouped like samples into distinct clusters. Thirty-six clusters offered a nice balance between adequate
common similarity within each cluster and the number of targets within a given cluster (see Figure 4.7). An iterative approach was applied (see Figure 4.8) and the lowest average similarity score (most similar groupings within all clusters across all iterations) was chosen as the result. Manual inspection of the results shows the algorithm paired many samples from within the same geologic formation/unit (see Table 4.2 and Figure 4.9). Despite a decreased weighting in dust-dominated elements like S and Cl, the script still separated as-is Burns formation targets from abraded Burns formation targets (Figure 4.9: compare Group 10, as-is, and Group 8, abraded). This speaks to not only the power of the script but also the high precision of the APXS. Variation in Cl and Br have been associated with aqueous processes - the resulting variation evident in the plots. Inspection of the automated cluster analysis supports a final, manual, reduction, as some clusters have similar compositional properties to others.

![Figure 4.7](image)

Figure 4.7: To determine the ideal number of clusters for the classification scheme, 100 iterations for each of 1 through 50 clusters were compiled. Solid line corresponds to the average cluster similarity score while dashed lines bound the observed range of the algorithm output. 36 clusters offers a balance between target similarity and a reasonable number of clusters.
Table 4.2: Group similarity score calculated as the average similarity score of all targets in a group by way of comparing each target to the average chemistry of the group. A lower score is indicative of being more-similar and thus is conducive to a more-similar group. Scores outlined in red correspond to groups that are weak in similarity. These internally less-similar groups are a mixture of targets that are unique but mathematically do not warrant their own group, or, are a group of targets (or a raster) that have varying abundances of unique compositional endmembers (e.g. Stuart Island). Colours provide a quick reference to the approximate similarity within a given group.

<table>
<thead>
<tr>
<th>Group</th>
<th>Targets</th>
<th>$S_{av}$</th>
<th>Notable Targets</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>0.86</td>
<td>Light-toned Soil</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>1.15</td>
<td>Pierre Pinaut</td>
<td>Marathon Valley</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>1.96</td>
<td>Grasberg</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>0.99</td>
<td>Lyell</td>
<td>Burns Fm.</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>0.70</td>
<td>Burns Fm.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>22</td>
<td>1.30</td>
<td>PRF, PSG, PJP, SRNP</td>
<td>Marathon Valley, Spirit of Saint Louis</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>0.95</td>
<td>LemonRind</td>
<td>Burns Fm. Abraded</td>
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<tr>
<td>8</td>
<td>8</td>
<td>0.72</td>
<td>Tennessee</td>
<td>Burns Fm. Abraded</td>
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<tr>
<td>9</td>
<td>13</td>
<td>1.13</td>
<td>Ripple Crest and Spherule-Rich Soil</td>
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</tr>
<tr>
<td>10</td>
<td>6</td>
<td>1.13</td>
<td>Guadalupe</td>
<td>Burns Fm.</td>
</tr>
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<td>11</td>
<td>9</td>
<td>3.27</td>
<td>Outlier Burns Fm. Abraded</td>
<td></td>
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<tr>
<td>12</td>
<td>24</td>
<td>2.23</td>
<td>Mix of Soil, Burns, Shoemaker, Grasberg</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>2.26</td>
<td>BerryBowl</td>
<td>Spherule-Rich Soil</td>
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<tr>
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<td>3</td>
<td>0.76</td>
<td>Salisbury</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>10</td>
<td>0.53</td>
<td>Lyell</td>
<td>Burns Fm. as-is</td>
</tr>
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<td>Ortiz</td>
<td>Vein-rich</td>
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<td>Juneau</td>
<td>Off-Nominal Soil</td>
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<tr>
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<td>Purgatory</td>
<td>Composite Soil</td>
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<td>Amboy</td>
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<tr>
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<td>0.68</td>
<td>Tinos</td>
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<td>SturgeonRiver, Fullerton</td>
<td>Shoemaker Fm., Matijevic Fm.</td>
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<td>1.31</td>
<td>Bounce Rock</td>
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</tr>
<tr>
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<td>0.84</td>
<td>Robert.E</td>
<td>Burns Fm. as-is</td>
</tr>
<tr>
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<td>Marquette</td>
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</tr>
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<td>14</td>
<td>1.74</td>
<td>Azilda</td>
<td>Matijevic Fm.</td>
</tr>
<tr>
<td>30</td>
<td>12</td>
<td>1.23</td>
<td></td>
<td>Burns Fm.</td>
</tr>
<tr>
<td>31</td>
<td>2</td>
<td>0.72</td>
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<td>Esperance Abraded</td>
</tr>
<tr>
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<td>0.52</td>
<td>Homestake</td>
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</tr>
<tr>
<td>33</td>
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<td>Tisdale</td>
</tr>
<tr>
<td>34</td>
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<td>2.25</td>
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<td>Mix of Marathon Valley Purple/Blue etc.</td>
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<tr>
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<td>0.74</td>
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<td></td>
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<td>36</td>
<td>6</td>
<td>1.69</td>
<td>Esperance</td>
<td>Esperance as-is</td>
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</tbody>
</table>

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Figure 4.8: Distribution of the average similarity scores for 36 clusters after 1,000 iterations. Classification scheme constructed from the lowest score which produced the clusters that are internally the most similar to their average.
Figure 4.9: Automated cluster groups sectioned by similarity score (chemistry) alone. Group 8 corresponds to Burns fm. abraded while Group 10 is as-is. Group 9 is spherule-rich soil while Group 18 is San Torini soil. Group 28 corresponds to Marquette targets while Group 36 to Esperance as-is. Clustering algorithm requires improvement due to potential bias to nearest-neighbours within $S$. 

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Chapter 5

Concluding Remarks

The APXS continues to provide high-value science while conducting X-ray spectrometry in a less-than-ideal operational environment. Despite the lengthy heritage and maturity of the APXS method, several advancements have expanded the capabilities of the APXS instruments active on the surface of Mars. These advancements further the capabilities of the instrument and better prepare the method for potential future missions where the focus and scientific goals may differ.

The ability to quantify chemistry for features smaller than the APXS FOV, on the sub-cm scale, presents a significant advancement in operational capability, especially with the MSL APXS. Geological features of high scientific interest are frequently encountered at scales smaller than the APXS FOV or of spatial structure where it is impossible to fill the APXS FOV with the feature. The post-launch conception and maturation of the APXS raster technique and associated algorithms to provide small-scale chemistry continues to be a powerful operational tool used by the APXS and MSL operations teams.

Measurements made by rastering with the APXS have offered high-impact results directly contributing to the scientific goals of the mission(s). A calcium sulphate vein provided the motivation and a perfect opportunity to test the raster deconvolution method on an ideal endmember, achieving fantastic results in the process. The deconvolution of dust from the high-Mn target Stephen provides more representative pure chemistry for the target of high scientific value. Deconvolved chemistry of a light-and-dark vein network features prominently in [49], with significant implications in terms of understanding past aquatic processes on the surface of Mars. The deconvolution of chemistry from two different nodules
on the surface of Mars - including the proper treatment of surface relief by immersing the APXS in a virtual 3D environment - also directly proves the past existence of an evolving fluid on Mars, or multiple fluid events. Achieving analytical APXS chemistry on the sub-cm scale for the first time has demonstrated its ability to unravel evidence with important implications for elucidating the formation mechanisms of various rocks on Mars. The method also facilitates the study of more heterogeneous targets with relevant instruments on Earth and has motivated the study of Martian meteorites with APXS and APXS-like methods at the University of Guelph.

The development of a simple layer model, constructed from physics fundamentals, opens the possibility to include deconvolution on a vertical scale in addition to the published work on lateral deconvolution. Furthermore, it demonstrates quite visibly the limitations of layer modelling given the range and importance of the various unknowns encountered when conducting measurements on the surface of Mars.

Rearranging the least-squares minimization algorithm at the core of the deconvolution routine facilitates compositional fitting of APXS measurements with known (or assumed) compositional endmembers. Modelling APXS compositions with pre-defined compositional endmembers permits the investigation into more-subtle chemical trends that may otherwise be hidden by the compositional noise associated with varying abundances of common endmembers like Martian dust or sulphates. The inclusion of a least-squares-determined endmember from an iterative analysis approach quantifies some of the variability within the very-homogenous Murray formation within Gale Crater and provides a level of insight into subtle changes not previously available.

Spectral simulations have proven important in both the published work and in preliminary results displayed for future tools. The radial sensitivity of the APXS was modelled to very close agreement with existing curves using a simple geometrical method. The empirical simulation of APXS spectra provides the opportunity to further understand APXS analysis tools as well as thoroughly examine the behaviour of the instrument.

Tools developed for the ease of quick comparison between samples within a large data base have been merged with a cluster analysis routine. Applied to the large abundance of MER-B targets, preliminary cluster analysis results shows promising behaviour using
strictly chemistry as a sorting mechanism. More development is required due to a slight nearest-neighbours bias in the current clustering script.

The detailed and methodical investigation into the large MER APXS atmospheric data collected has probed the physics of the MER APXS instrument within its environment, and also prompted some possibly interesting discoveries in atmospheric science. Through careful investigation of atmospheric spectra, using primarily the argon peak, the ideal gas law is verified to great ($R^2 = 0.95$) confidence thereby proving the method and data analysis. Summation of over 1,600 hours of good-temperature atmospheric data provides the clearest picture of the spectral background experienced by the MER APXS instruments. All signals are dispositioned with the exception of a spectral shelf terminating at around 3.5-3.75 keV.

Lastly, when comparing the argon density measurements made over several Mars years by the MER-B APXS against previous pressure-measuring spacecraft situated near the equator, there is fantastic agreement in the relative changes in argon density amplitude via the APXS with relative changes in pressure observed by the other spacecraft. There is a slight shift in timing, potentially providing evidence to the atmospheric mixing timeline at the Martian poles. Most interestingly, there is a spike in argon density measured during the massive flux of CO$_2$ after sublimation from the southern polar cap back into the atmosphere. The sharp-but-brief rise in argon density is consistent from year to year and statistically real. Orbiting argon-detecting instruments are unable to detect changes in argon at the scale observed by the MER APXS. The MSL pressure monitoring instrument did detect changes in pressure consistent with a 5-10% jump in non-condensable gasses (like argon). The observed mixing ratio is in agreement with previous work and measurements made at Gale Crater with the SAM instrument. However, due to the terrain effects, it is unlikely SAM will be able to resolve the spike observed by the MER-B APXS. There is also evidence for a southbound spike in argon from the northern cap region. The observation warrants a detailed study with the MER-B APXS.
Bibliography


