INVESTIGATION OF TRACE ELEMENT CONCENTRATIONS IN SUMMED SPECTRA FROM THE MARS EXPLORATION ROVER ALPHA PARTICLE X-RAY SPECTROMETERS. A. L. Knight[1*], S. J. VanBommel[1], R. Gellert[2], J. G. Catalano[1], J. A. Berger[3], and J. Gross[3,4], [1]Dept. of Earth & Planetary Sciences, Washington University in St. Louis, St. Louis, MO; [2]University of Guelph, Department of Physics, Guelph, Ontario, Canada; [3]NASA Johnson Space Center, Houston, TX; [4]Dept. of Earth & Planetary Sciences, Rutgers University, Piscataway, NJ; [*]alknight@wustl.edu.

Background: The Mars Exploration Rovers (MER) *Spirit* (MER-A) and *Opportunity* (MER-B) were each equipped with an Alpha Particle X-ray Spectrometer (APXS) as part of their scientific suite of instruments. The APXS interrogated rock, regolith, and soil targets at both landing sites (Gusev Crater and Meridiani Planum, respectively) and ultimately quantified major, minor, and trace element abundances in targeted materials [1]. The MER APXS determines the composition of martian materials primarily through a combination of particle-induced X-ray emission (PIXE) and X-ray fluorescence (XRF) analyses, the ratio of which depends upon the atomic number of the element of interest. The APXS bombards the target with alpha particles and X-rays emitted from the decay of curium-244 to plutonium-240 [1,2]. Emitted X-rays and alpha particles can induce characteristic X-rays within a target, which are subsequently detected by the APXS's silicon drift detector. This is the analytical method at the focus of this work, as it provides a reliable means to quantify, with high precision, elements of atomic number ≥ 11 (i.e., Na and heavier) [1].

The detected characteristic X-rays are tabulated into an energy-dispersive spectrum, essentially a histogram of detected X-rays with the bin width referred to as the gain (eV/channel). All MER APXS spectra are available in the public domain via NASA's Planetary Data System (PDS) [3]. The archived data additionally include relevant metadata pertaining to experimental conditions, such as temperature and measurement duration. These factors, alongside the varying spectral background, the proximity of the APXS to a target, and the age of the mission (via source activity and detector resolution), all affect APXS quantifications.

Purpose: To date, sixteen elements have been quantified and published for each MER APXS target in the PDS [4]. However, limited results exist for many trace elements, including Cu, Ga, and Ge, in the literature. These trace elements and their ratios to other major (e.g., Al and Si) and trace (e.g., Zn) elements can be used as tracers of past aqueous activity on Mars [5]. Published quantifications of Ge at Meridani and Gusev have been rare and restricted to high concentration (≳850 μg/g) targets [6,7], but quantification of Ge at much lower concentrations (<30 μg/g) could further inform a myriad of geologic questions (e.g., [8]).

At first order, peak areas in APXS spectra scale with elemental abundance in a target, thus quantifying low abundance elements has posed a challenge in the past due to a low signal-to-noise ratio. Smaller peak areas overlap with other element lines, and in some cases, high background (e.g., the Cu background from the copper-beryllium doors and other APXS hardware [9]) contribute to the challenge of quantifying trace elements. Any model seeking to accurately quantify low-abundance elements of an APXS spectrum must account for the varied experimental conditions encountered by *Spirit* and *Opportunity* throughout their missions [1,2,10]. In general, lower temperatures, decreased standoff, and longer measurement times improve counting statistics and the ability to resolve peaks. Spectra acquired at substantially high temperatures should be removed from the dataset because they are prone to degraded spectral resolution. Spectra should also be normalized to account for the variation in counting statistics and background due to their varied standoff, mission age, and total measurement time to give a more accurate relative comparison.

For many trace elements, especially at low concentrations, the counting statistics of individual spectra remain too poor to quantify their abundances with confidence (i.e., <20% precision uncertainty). In this work, we have taken a novel approach to precisely quantifying MER APXS trace elements at low (<30 μg/g) concentrations by creating a library of *composite* spectra with superior counting statistics compared to individual spectra. Each individual APXS spectrum was classified and summed with others based on one or more shared characteristics, such as location, target, and/or target type (e.g., rock or soil). Individual spectra were filtered to account for possible contaminants (e.g., pebbles in soil) to achieve the cleanest possible spectrum. In turn, the relational spectral library ultimately facilitates the summation of MER spectra based on numerous user inputs. The resulting composite spectra benefit the quantification and analysis of trace elements by potentially enabling the derivation of new trace element results at lower limits.

Methods: All spectra were retrieved from the PDS, processed, and filtered. The filtered spectra were then used to develop a simplified fit routine to model experimental conditions encountered by *Spirit* and

Opportunity throughout their respective missions. All spectra were tied to classifications related to location, feature, target, target type, site, and the level of sample preparation (i.e., abraded, brushed, or as-is). Filtered spectra were then summed based on their shared characteristics and locations to improve counting statistics. From these composite sum spectra, proxies were derived for the concentrations of Cu, Ga, and Ge at low abundances.

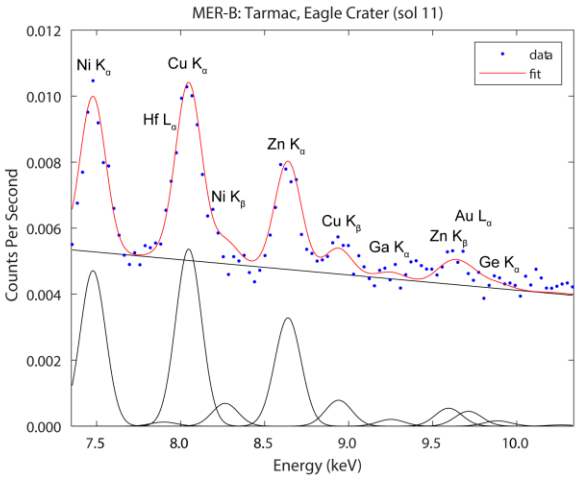

Figure 1: Spectrum and fit of Eagle Crater target "Tarmac", acquired by *Opportunity* on sol 11. The signal to noise is too low to quantify Ga and Ge in particular.

Analysis: Individual filtered spectra for MER-A and MER-B have average measurement times of ~5.7 hours. The first soil measurement *Opportunity* acquired ("Tarmac," located in Eagle Crater) had a reasonable measurement duration of ~7.6 hours (Figure 1). This spectrum is representative of an early mission individual analysis with respect to measurement time, counting statistics, and trace element concentrations. Operational limitations made the acquisition of such statistics in a single activity more challenging, especially late in *Opportunity*'s mission, thus potentially complicating the quantification of some trace element concentrations.

Summing spectra based on their shared characteristics increases total measurement time, improves counting statistics, reduces noise, and in this same example, resulted in well-resolved trace element (e.g., Ga and Ge) peaks (Figure 2). Proxy uncertainties decreased (now ~15-20%) after summing appropriate spectra from Eagle Crater, and distinct peaks can now be identified within the composite sum spectrum.

Continued Work: All collections of summed spectra will be inspected for the presence of distinct trace element (e.g., Cu, Ga, and Ge) peaks. These collections will then be analyzed to obtain concentrations of these (and other) trace elements, providing quantifications for specific geologic regions at Meridiani Planum and Gusev Crater. The resulting elemental abundances will be combined with published oxide concentrations to provide novel insight into local and global geochemical processes recorded along the MER traverses. These concentrations can then be used to achieve objectives such as identifying hydrothermal units at Endeavour crater, characterizing silica-rich deposits in Gusev crater, and elucidating the provenance of Mars soils.

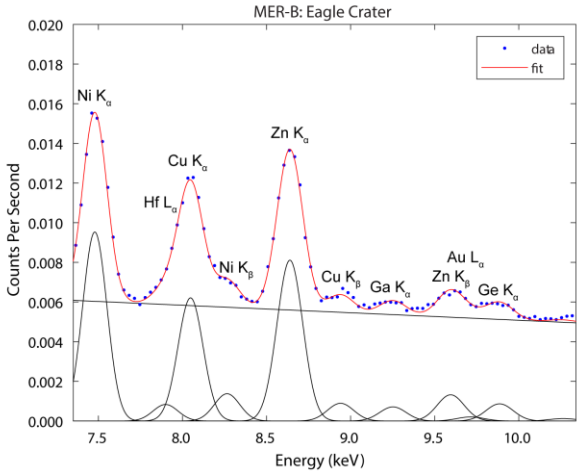

Figure 2: Spectrum and fit of the processed, filtered, and summed spectra of related Eagle Crater targets. Total measurement time of the 14 combined spectra is ~79.7 hours.

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