PRELIMINARY ANALYSES OF SELECT TRACE ELEMENT ABUNDANCES FROM THE MARS EXPLORATION ROVER ALPHA PARTICLE X-RAY SPECTROMETERS. A. L. Knight[1] and S. J. VanBommel[1], [1]Department of Earth & Planetary Sciences, Washington University in St. Louis, St. Louis, MO, 63130 (alknight@wustl.edu; vanbommel@wunder.wustl.edu).

Introduction: The Alpha Particle X-Ray Spectrometers (APXS) on the Mars Exploration Rovers (MER) *Spirit* (MER-A) and *Opportunity* (MER-B) measure induced X-rays obtained from the interrogation of geologic materials by complementary particle-induced X-ray emission (PIXE) and X-ray fluorescence (XRF). The resulting histogram of observed X-ray energy quanta (a spectrum; e.g., [1]) is subsequently analyzed in order to quantify elements (e.g., [2]) as a function of their peak areas [3].

The abundance of major, minor, and several trace elements in martian materials obtained from APXS measurements are available in the Planetary Data System (PDS) [2]. Trace element concentrations reported for every sample include Ni, Zn, and Br. Other trace elements, such as Cu, Ga, and Ge, are important geochemically because quantification of these additional trace elements and their ratios to other oxides may provide insight into past magmatic and aqueous processes on Mars (e.g., [4]). Of these three trace elements, Cu has a particularly large background due to both the copper-beryllium doors on the face of the APXS instrument and Cu in the hardware surrounding the detector [5]. Additional trace element concentrations, (e.g., Cu, Ga, and Ge) obtained by the MER APXS are of limited availability in the public literature at present.

APXS analytical capabilities for trace elements are dependent on the experimental conditions. Improved performance (lower detection and quantification limits) is achieved with longer measurement times, closer proximity to the sample, and colder temperatures [6]. Specifically, the precise quantification limit (PQL) of trace elements decreases with increasing measurement time. The MSL APXS PQL values determined for Ge, Ga, and Cu for an 8 hour measurement under ideal conditions are 25, 25, and 30 ppm, respectively [6]. PQLs on MER are higher due to, in part, the configuration and activity of the ^{244}Cm sources and instrument architecture (i.e., minimum standoff distance of 30 mm cf. 18 mm on MSL).

In addition to changes in target chemical composition, variation in APXS spectra also reflect changes in experimental conditions [3, 7, 8]. APXS data acquired on MER-A and MER-B targets include measurement durations with a range of more than an order of magnitude, resulting in significant variation in counting statistics. The temperature at the time of data acquisition affects the energy resolution of the spectra; higher temperatures result in peak broadening that must be accounted for to accurately deconvolve overlapping signals and peaks [7, 8]. The proximity of the APXS instrument to the target also affects spectral count rates and the observed background. With increasing standoff, the total counts from a sample decreases. Each of these experimental variables must be incorporated into any analysis routine to accurately model and thus quantify the signal corresponding to each element, in addition to the subtraction of any known background signals.

Here we present preliminary work that follows the method of [6, 7] with the ultimate goal of improving the detection limits of trace elements in MER APXS data. Upon completion of the project, the results obtained could enable new, precise, quantifications of select trace elements, such as Ge, Ga, and Cu, in targets or broader geologic units at both Gusev and Meridiani.

Methods: Analyses of MER APXS spectra have evolved since the onset of the project, incorporating additional experimental parameters and physics fundamentals with each iteration. The analysis routine from which the results herein were derived considers multiple parameters, in a global context where appropriate.

APXS spectra from [1] were processed and ultimately used to produce a simplified model that was applied across all measurements conducted by both rovers. At present, we derive a proxy for the concentrations of Ni, Cu, Zn, Ga, and Ge. For Ni and Zn, with reported abundances available from [2, 3], the derived proxies herein were able to be compared (Figure 1), ultimately providing confidence in the derived for Cu, Ga, and Ge abundance analogs. Deviation from an ideal linear response is expected due to matrix effects (attenuation of characteristic X-rays by the sample itself), which are not mitigated in the current concentration proxy framework.

Analysis: The calculated Ni and Zn concentration proxies are consistent with derived concentration values and show a positive linear correlation, indicating a successful estimate of trace element signal by the current model (Figure 1a, Figure 1b). Analyses of the locally processed spectra prompted the identification of targets with exceptionally high concentrations of some trace elements (e.g., Figure 2). Plots of trace element

concentration proxies as a function of sol provide a quick means to visualize enrichments along the respective traverses.

Most notable of the enrichments observed, around sol B4000, *Opportunity* encountered targets suggestive of significant Ge enrichment [9, 10]. From a preliminary assessment, and a very crude conversion of proxy to physical concentration, the Ge values in this region are estimated to reach in excess of 750 µg/g. This estimate is consistent with other studies (i.e., [9, 10]) that utilized conventional spectral analysis techniques (i.e., [3, 8]).

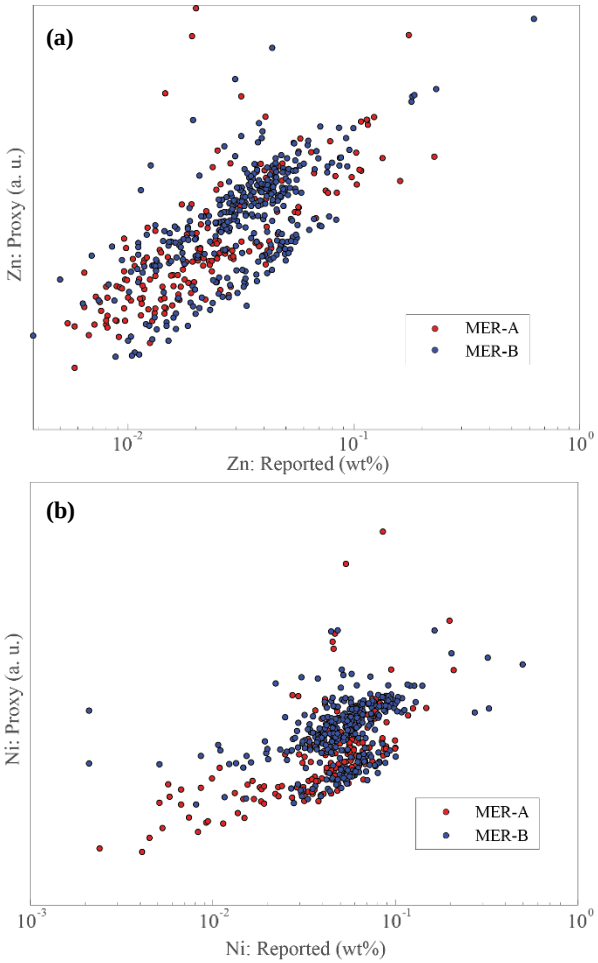

Figure 1: Derived (a) Zn and (b) Ni abundance proxy for MER-A and MER-B compared with those reported in the public domain. Scatter can largely be attributed to matrix effects, mitigated in the reported concentrations (e.g., [3]) but not in the proxy values, and an incomplete analysis model. Uncertainties are not plotted as to not obfuscate the data. Reported concentration uncertainties are available in [2]. Proxy uncertainties were typically 15-20% relative.

Future Work: Continued advancements to the analytical model will be made as additional capabilities are added and the general accuracy is improved. Techniques utilized in [6, 7, 11] will be applied to lower the detection limits and could ultimately either a) provide trace element concentration results for the first time, or b) provide an improved upper limit of select trace elements in these samples and regions. The abundance and distribution of additional trace elements beyond those noted herein will also be studied.

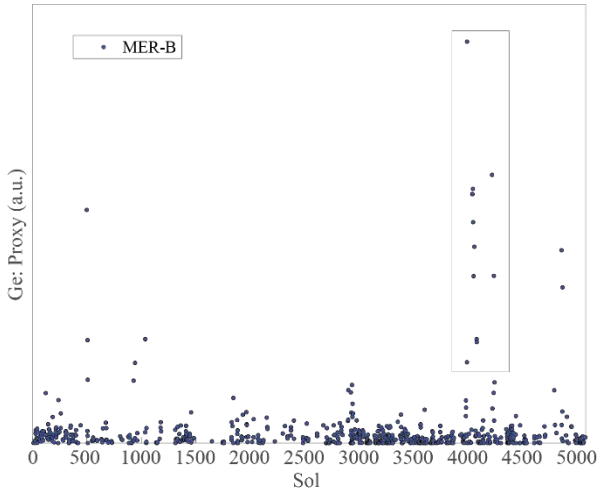

Figure 2: Inferred Ge abundances by sol for MER-B. Enrichments of several hundred µg/g are inferred in samples around sol 4000 (outlined). Other studies (i.e., [9, 10]) have quantified enrichments of ≳850 µg/g in this region.

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References:

[1] Planetary Data System, APXS Partially Processed Data, dois: 10.17189/1518981, 10.17189/1519001.
[2] Planetary Data System, APXS Derived Data, doi: 10.17189/1518973.
[3] Gellert et al., (2006), JGR, 111.
[4] Berger et al., (2017), JGR, 122.
[5] VanBommel et al., (2018), JGR, 123.
[6] VanBommel et al., (2019), Acta Astro., 165.
[7] VanBommel et al., (2019), NIM:B, 441.
[8] Rieder et al., (2003), JGR, 108.
[9] Mittlefehldt et al., (2016), LPSC XLVII, 2086.
[10] Mittlefehldt et al., (2021), JGR, Submitted.
[11] VanBommel et al., (2021), this conference.