ANALYSIS OF TRACE ELEMENT CONCENTRATIONS BY THE MARS EXPLORATION ROVER ALPHA PARTICLE X-RAY SPECTROMETERS: IMPLICATIONS FOR DIAGENETIC FLUIDS AT MERIDIANI PLANUM AND GUSEV CRATER. A. L. Knight[1], S. J. VanBommel[1], R. Gellert[2], J. A. Berger[3], J. G. Catalano[1], and J. Gross[4,5], [1]Dept. of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, MO; [2]Dept. of Physics, University of Guelph, Guelph, Ontario, Canada; [3]Jacobs JETSII at NASA JSC, Houston, TX; [4]NASA JSC, Houston, TX, [5]Dept. of Earth and Planetary Sciences, Rutgers University, Piscataway, NJ.

Introduction: The Alpha Particle X-ray Spectrometers (APXS) onboard the *Spirit* and *Opportunity* rovers interrogated the bedrock, soil, and regolith at Gusev crater and Meridiani Planum, respectively. The APXS utilized both particle-induced X-ray emission (PIXE) and X-ray fluorescence (XRF) spectroscopy to assess the elemental composition of a sample [1, 2]. The resulting detected X-rays form a histogram (i.e., spectrum) of energies with bin widths of ~32 eV. Characteristic peak areas, increasing with elemental abundance for a given element, provide the primary means for composition determination [1, 2].

On Mars, experimental conditions are variable and impact acquired spectra. Several factors, such as mission age, measurement duration, distance between target and detector (i.e., "standoff"), and temperature alter acquired spectra which, in turn, can impede precise quantification of some elements [1-3]. Furthermore, a single APXS measurement often yields insufficient counting statistics to precisely quantify trace elements at low (<30 μg/g) concentrations, such as Ga and Ge. By summing similar spectra together to create a *composite* spectrum, however, one increases the counting statistics and signal-to-noise ratio, thus enabling greater precision in the quantification of trace elements at lower concentrations than previously possible.

Trace elements can provide constraints on the geologic history and diagenetic fluids that have altered the rocks in a region (e.g., [4-6]). *Spirit* and *Opportunity* investigated many locations and formations within Gusev crater and Meridiani Planum that possessed indicators of past diagenetic alteration (e.g., [7-9]). At Meridiani Planum (in order of increasing age) these include the Burns, Grasberg, Shoemaker, and Matijevic formations. The Burns formation is a sulfate-rich sandstone that has been altered by diagenetic fluids, producing jarosite and spherules of hematite [7,10-12]. The Grasberg and Matijevic formations are likely distant volcanic or impact ejecta deposits [13], and the Shoemaker formation (subdivided into the upper and lower Shoemaker units) is thought to be impact ejecta from multiple distinct craters [14]. At Gusev crater, *Spirit* investigated outcrops of volcanic material displaying evidence of diagenetic alteration. The objective of the work herein is to quantify the concentrations of Ga and Ge in composite spectra from formations at Meridiani Planum and locations at Gusev crater and assess the implications for the geologic and diagenetic histories of these regions.

Methods: Spectra were acquired from the Planetary Data System (PDS) [15], processed, and filtered to remove temperature-degraded spectra. The characteristics of each APXS measurement, such as degree of sample preparation (e.g., as-is, brushed, abraded), location, feature, target, formation [14] and target type (e.g., rock, soil) were assigned to each spectrum. Individual spectra were then summed based on shared characteristics to create a composite spectrum with improved counting statistics. Composite spectra of interest were identified with a simplified nonlinear least squares fitting routine composed of Gaussian peaks on a linear background. Individual spectra comprising a composite spectrum were visually and quantitatively inspected to confirm that the composite spectrum was representative of the individual spectra and not a reflection of outliers. Additionally, statistical confidence in the presence of legitimate trace element peaks in the composite spectrum was obtained with a log-likelihood ratio test comparing observed spectra to "trace-element-free" spectra with Poisson noise artificially added. Select composite spectra with promising trace element peaks were fit by the standard fitting routine used to quantify other elements (e.g., [16]) present in individual APXS spectra [1].

Results: Summing like spectra together resulted in increased counting statistics and well-resolved trace element peaks. The trace element peaks noted in the composite spectra were determined with >99% confidence to not be a manifestation of Poisson noise. Additionally, composite spectra assessed herein are composed of similar individual spectra and do not contain outliers (e.g., Figure 1). Based on the composition of CI chondrites [17], concentrations of Ga and Ge are more than an order of magnitude greater than expected from meteoritic input alone. In addition, the molar ratios of Ga to Al are relatively consistent across formations at Meridiani Planum, whereas the molar ratios of Ge to Si are much more variable. In addition to the Ge to Si ratios, the concentrations of Ge are elevated in the Burns and Grasberg formations compared to the older Shoemaker and Matijevic formations (Figure 2).

Discussion: The elevated concentrations of Ga and Ge in outcrops at Meridiani Planum and Gusev crater relative to expected values from the composition of CI chondrites and elemental ratios suggest that meteoritic input alone would be insufficient. The widespread (e.g., distant impact ejecta) and variable origins of each of the formations at Meridiani Planum also suggest that a global phenomenon (e.g., volcanic outgassing [18]) may be responsible for the high concentrations of volatiles (including Ge). The relatively consistent ratio of Ga to Al across Meridiani Planum formations may be explained by high temperature diagenetic fluids. At ~25 °C, Ga speciation is largely dominated by $Ga(OH)_4^-$, but Al is predominantly in the form $Al(OH)_3^0$, leading to differences in solubility of these two elements [19]. However, at higher temperatures, the solubilities of Ga and Al converge for acidic-to-neutral pH values [19]. Likewise, the divergence in geochemical behavior of Ge and Si may be the result of high temperature fluids because the volatility of Ge enables it to concentrate more effectively relative to Si at high temperatures. The youngest formations at Meridiani Planum also contain the highest concentrations of Ge, which may suggest that alteration was more prominent in the uppermost strata of Meridiani Planum.

Conclusion: A database of target characteristics for each APXS rock, soil, or regolith measurement has been assembled and utilized to create a series of composite spectra. Quantifications of Ga and Ge in select composite spectra indicate that meteoritic contributions alone are insufficient to account for the concentrations of these trace elements in outcrops at Meridiani Planum and Gusev crater. A small meteoritic component supplemented by a much larger volcanic outgassing component could supply some of the excess volatile concentrations, which may then have been further concentrated by regional high temperature diagenetic fluids.

Acknowledgments: All data utilized are publicly available on the Planetary Data System [16, 17]. The authors thank all who contributed to the development and execution of the MER mission, including members of NASA/JPL and the MER team. This work was supported by NASA MDAP grant #80NSSC20K0939.

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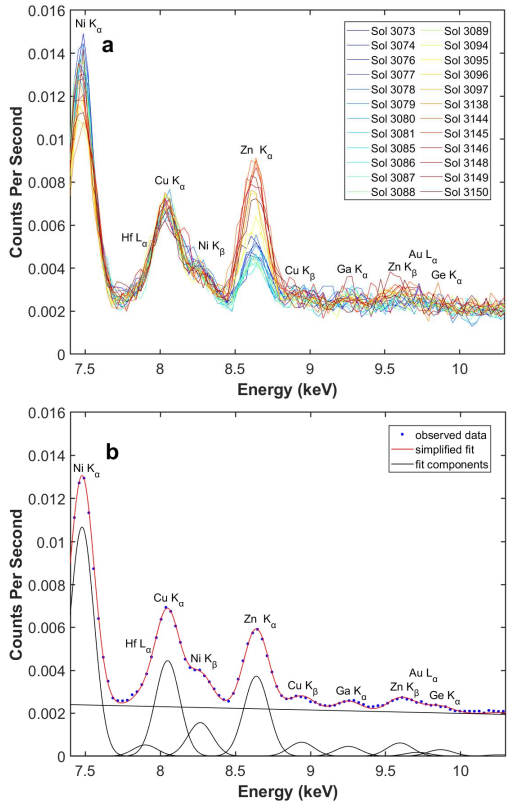

Figure 1. Processed and filtered (a) individual spectra comprising the (b) composite spectrum and simplified fit of the APXS rock targets within the Matijevic formation, as defined by [14].

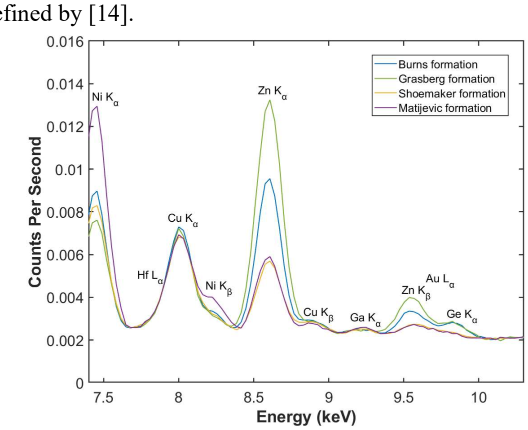

Figure 2. Composite spectra of geologic formations interrogated by *Opportunity* at Meridiani Planum. Spectra have been count-normalized for direct visual comparison.