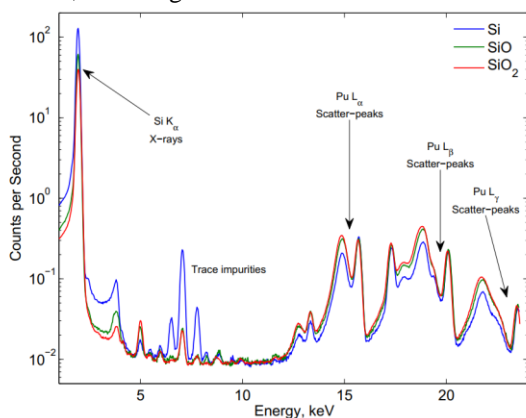


**QUANTIFICATION OF INVISIBLE ELEMENTS AND LAYERING EFFECTS WITH THE MARS SCIENCE LABORATORY ALPHA PARTICLE X-RAY SPECTROMETER.** J. U. Hanania<sup>1</sup>, R. Gellert<sup>1</sup>, B. J. Wilhelm<sup>1</sup>, and S. J. VanBommel<sup>2</sup>, <sup>1</sup>University of Guelph, Guelph, ON, Canada, <sup>2</sup>Washington University in St. Louis, St. Louis, MO, USA

**Introduction:** The Mars Science Laboratory's (MSL) Alpha Particle X-ray Spectrometer (APXS) has been operating on the surface of Mars since August 2012. The APXS is capable of determining the chemical composition of rocks and soils on Mars through the primary mechanisms of X-ray fluorescence (XRF) and particle-induced X-ray emission (PIXE) [1,2]. XRF and PIXE produce characteristic X-rays from elements within the sample, beginning with Na. These X-rays of rock-forming elements typically range in energy from 1 keV to 12 keV and thus occupy the lower-energy half of a MSL APXS spectrum (Figure 1). The latter half of the energy range comprises signals from the spectral background as well as backscattered plutonium L X-rays created during the decay of the APXS curium-244 sources. Scatter-peak intensity depends on the target composition (including elements lighter than Na), standoff (distance between the target and a contact-sensing plate affixed to the front of the APXS), temperature, and integration time.



**Figure 1.** Three overlaid APXS spectra from Si-rich laboratory samples. Figure from [3].

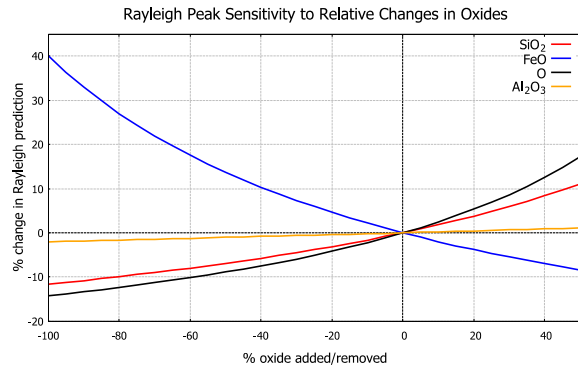
**Motivation:** Insight into light element abundance and potential sample hydration supports more accurate geological interpretations of Gale Crater, Curiosity's landing site. Past work (e.g. [3,4]) has investigated the use of X-ray scatter-peaks measured by the APXS to quantify "invisible" elements (light elements ranging from H to Ne, which typically cannot be measured through the primary APXS analysis mechanisms). Figure 1 displays three Si-rich APXS spectra overlaid, differing only in the abundance of bound oxygen. The increase in oxygen acts to amplify intensities of scatter

peaks, more so the inelastic (Compton) peaks which make up the broader, left, peak of each doublet. The theoretical inelastic/elastic (Compton/Rayleigh, C/R) ratio is compared to the measured C/R ratio for a given target. Any difference is attributed to an excess or deficit of invisible elements (e.g. bound oxygen, carbon, H<sub>2</sub>O).

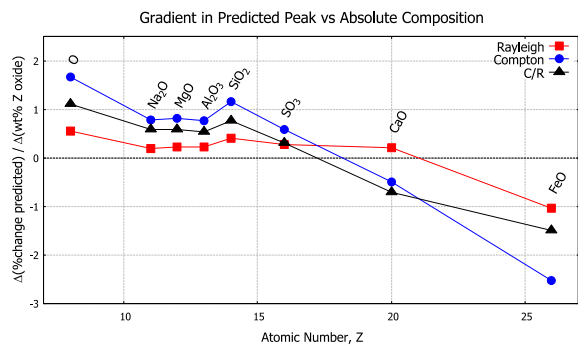
Limitations in this analysis arise from the simultaneous use of both Compton and Rayleigh peaks. First, the use of both elastic and inelastic peaks introduces considerable error bars for the light elements as both peaks have a given statistical uncertainty. Additionally, the absolute count rate of the peaks is lost through the ratio. To resolve these limitations, this work treats the Compton and the Rayleigh peak in isolation. Individual peak analysis reduces uncertainty and retains information in regards to absolute intensity. The magnitude of scatter peak intensity permits standoff quantification without requiring normalization to 100% as in typical APXS analyses. Moreover, the possibility to quantify layering within targets is available through analysis of all three scatter-peak doublets.

**Scatter-Peak Sensitivity:** Understanding scatter peak sensitivity to changes in composition provides modelling constraints for various applications discussed below. Analytically calculated scatter peaks permit the rapid assessment of theoretical scatter-peak intensities for a specified composition. Figure 2 and Figure 3 demonstrate various sensitivities in L<sub>α</sub> scatter-peak intensities with a varied Martian soil (Sourdough, sol 673) composition. Figure 2 captures the relative change in Rayleigh peak for the defined variation in analyte abundance, ranging from 100% removal to 50% relative addition (sample composition was renormalized for each iteration).

Since Figure 2 biases oxides that make up most of the composition, Figure 3 captures the effect of the absolute addition of oxides in order to remove this bias. It is shown as the gradient of the sensitivity, in units of % change in the predicted peak per added wt% of the oxide, plotted against atomic number, Z. Figure 3 illustrates that scatter peaks are most sensitive to changes in oxygen and iron. Inelastically scattered Compton X-rays are more than twice as sensitive to composition compared to their elastic counterpart.



**Figure 2.** Predicted Rayleigh peak with compositional changes (e.g. accuracy errors); abscissa ranges from full removal of oxide to addition of 50%.

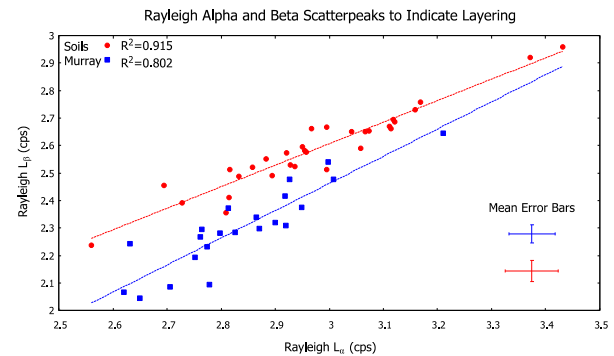


**Figure 3.** Sensitivity gradient values for absolute alterations of major oxides about the actual composition of Mars soil target Sourdough.

**Discussion:** Several capabilities can be employed when shifting from the relative to absolute analysis of the scatter peaks. The use of absolute scatter-peak intensity facilitates a direct measure of instrument stand-off. Rayleigh peak prediction models have been developed for cases where the stand-off estimated from APXS characteristic peak totals differs from the stand-off calculated using the Rayleigh peak. In such a scenario, the theoretical Rayleigh peak is altered by adding or removing invisibles so the prediction matches experiment.

Another capability of absolute peak analysis is to provide insights into layering within a sample. The APXS emits three primary plutonium L X-rays ( $L_{\alpha}$ ,  $L_{\beta}$ ,  $L_{\gamma}$ ), resulting in three Compton-Rayleigh doublets within an APXS spectrum (Figure 1). Higher energy X-rays probe deeper into samples on average and thus any differences between measured and predicted values may imply the presence of layering within the sample. For Mars soils, which are effectively homogenous, little layering effects are seen in practice (Figure 4, red line). Samples measured in the Murray formation (Figure 4, blue line), show more variability between the  $L_{\alpha}$

and  $L_{\beta}$  peaks, potentially indicative of compositional layering. Modelling of these effects is ongoing.



**Figure 4.** Experimental Rayleigh peak comparison for Martian soils and Murray targets (corrected for time and standoff).

**Conclusion and Outlook:** A detailed characterization of APXS scatter peaks will ultimately facilitate the implementation of an iterative scatter-peak-analysis routine into the core APXS spectral analysis program. Currently, APXS analyses assume measured elements are bound as oxides in pre-determined stoichiometric ratios. This is a valid assumption for unaltered geologic samples without significant invisible light elements. After bound oxides are assumed, the composition is simply normalized to 100% [1]. With the incorporation of scatter peaks, the oxide assumption and normalization could be avoided, with the presence of invisibles satisfying the closure rule. Such a quantification of invisible components requires an iterative calculation of the composition with matrix effects adjusted for each determination of invisibles.

**References:** [1] Gellert R. et al. (2006) *JGR*, 111. [2] Gellert R. and Clark B. (2015) *Elements*, 11(1). [3] Tesselaar D. (2015) *M.Sc. Thesis*. [4] Campbell J. L. et al. (2007) *JGR*, 113.

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