Systematic Error and the Identification of Minor Phases Using the CheMin X-Ray Diffractometer.

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Introduction: The CheMin XRD is the premier mineralogical identification tool on the Mars Science Laboratory mission exploring the geologic history of Gale crater [1]. The instrument has been used to successfully determine the mineralogical content of Martian drill and scoop samples, providing critical context in constraining their paleo-environments and later episodes of aqueous alteration [2-6]. Recent improvements in the data reduction methods have greatly enhanced the accuracy and precision of CheMin mineralogical interpretations [7, 8]. The potential importance of minor phase (<5%) identification by CheMin in scientific interpretation has motivated us to perform an error analysis of both the raw data and the reproducibility of the mineralogical interpretations to help evaluate at what level of confidence specific minor phase detections and abundances should be regarded.

Analysis Method: The physical design of the instrument and the standard data reduction method are well known [1]. In brief, the CheMin instrument uses a Co-Kα X-ray source to measure powder diffraction peaks in transmitted geometry using a 2D detector. Raw data is processed onboard the rover to produce diffraction data products which are returned to Earth. On Earth, data from each night of ~8hr of analysis are summed into units referred to as major frames; a typical analysis consists of 3 major frames. All of the major frames from a given analysis are de-spotted by hand, then summed and linearized. Mineral abundances are calculated via Rietveld refinement using the Jade software package (v. 10, MDI) and mineral information from the American Mineralogist crystal structure database. Different abundances of major mineralogy among human fitters are accounted for by simple averaging. Minor phase identification is determined by consensus, largely based on the confidence with which a minor peak can be distinguished by eye from the background noise and uniquely correlated with a plausible mineral.

Error Analysis: The Confidence Hills drill sample presents an interesting opportunity for statistical analysis as 5 major frames of data were collected [9] (Fig. 1). To determine the intrinsic instrumental uncertainty (scatter) associated with a major frame of data, we calculated the average magnitude of scatter in a nominally linear portion of the diffraction pattern free from diffraction peaks. The relative magnitudes of the systematic and random components of the scatter were determined by examining the limit of the improvement of the scatter with increased analysis duration (Fig. 2). The 2θ dependence of the random component of the scatter was evaluated using the deviation of each major frame from the average and demonstrated that the random scatter is dominated by a nearly constant level of absolute (rather than relative) scatter, although increased scatter is associated with the major diffraction peaks and very low-angle scatter. A Fourier transform of the data shows no strong correlation between the scatter and any particular interval of 2θ angle, making identification of the source of non-random scatter difficult.

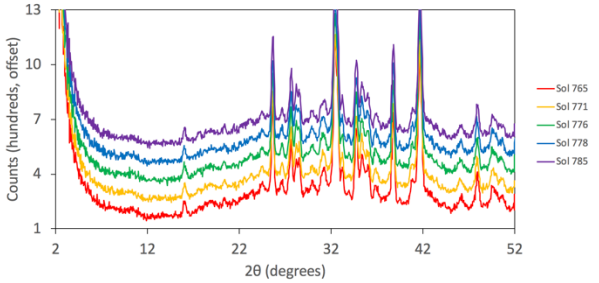

Figure 1: Confidence Hills major frames (offset by 100 counts/ea).

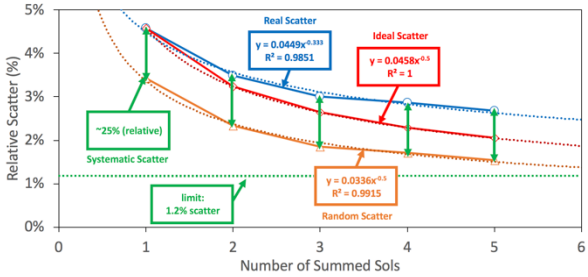

Figure 2: Evolution of background scatter with increased analysis duration between 11.7-15.6° 2θ. The non-ideal relation between the amplitude of the scatter and analysis duration indicates a non-random component of the scatter of ~1.2% of the total counts, or ~25% of the total scatter associated with a single major frame.

Rietveld refinement of the diffraction data was approached through six distinct rounds of fitting (Fig. 3). Fitting started with a highly restricted case where the background and mineral lattice parameters were fixed to a 'best-fit' value from fitting the full diffraction pattern. Each subsequent round added more variables that were fit independently for each minor frame rather than relying on 'best-fit' values from the full dataset. The most obvious effect is a systematic increase in predominantly minor phase abundances (with accompanying decrease in major phases) in later rounds. This effect is almost entirely due to misfit of the background curve, which varies substantially from ideal due to a significant amorphous component, which the automated fitting algorithm employed in Jade doesn't model well.

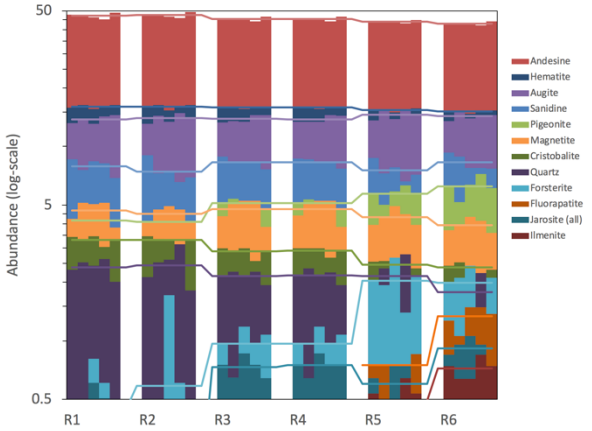

Figure 3: Phase abundance histogram showing fits to each sol across all six rounds. Each round increased the number of parameters independently fit, such that the first round applied parameters from a 'best-fit' model and the last independently fit all parameters. The method employed here diverges significantly from the standard analysis method and includes a number of phases in the fitting process that are questionably detectable – these results are for statistical analysis, not a revised composition of the CH drill sample.

If there was no overlap between mineral diffraction peaks the limit of detection (LoD) would be a peak amplitude above the level of the background scatter, ~ 10 counts in a major frame, with a limit of quantification (LoQ) 3x LoD. Due to the pervasiveness of overlapping diffraction peaks, integrated peak areas should be considered instead.

A good example of a quantifiable minor phase in the CH sample is quartz. Quartz was consistently fit in all six rounds of fitting with an abundance of ~2 wt%. The principal peak for quartz is {0 1 1} at 31° 2θ, which is easily discernable in the diffraction pattern (Fig. 1). This peak overlaps with low-amplitude peaks from plagioclase, sanidine, augite, and pigeonite (Fig. 4). The total uncertainty that the quartz detection must overcome is therefore a factor of not just the baseline scatter, but also the uncertainty in the intensity of the overlapping peaks. Furthermore, there is considerable uncertainty in how the background is fit in this portion of the CH diffraction pattern (Fig. 4). The integrated residual peak area (after subtracting for these factors) is 33.7 with an associated uncertainty of ±3.8 from overlapping peaks and the background position, compared to the integrated scatter estimate of 6.3 over the same interval. This quartz peak is above both the LoD and the LoQ, even after accounting for the uncertainty from overlapping peaks.

A more difficult example is the potential detection of jarosite, which is consistently fit as below 1 wt% of the total crystalline phases. The strongest diffraction peak for jarosite is {1 1 3} at 33.8° 2θ. None of the major mineral phases have peaks that overlap with this jarosite peak, limiting their effect on the uncertainty. The integrated peak area of this jarosite peak is 12.9 with an associated uncertainty of ±1.5 from the background position. By comparison, the integrated background scatter is 5.6 for the same interval, which makes jarosite above the LoD, but below the LoQ.

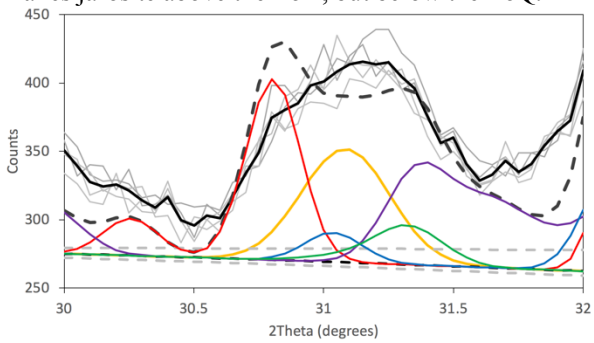

Figure 4: Comparison between the observed peak (major frames gray, average black), average background fits from different rounds of fitting (dashed), and the fit peak (gray, dashed) for quartz. Peaks from individual minerals are shown: quartz (yellow), feldspars (red, purple), pyroxenes (green, blue).

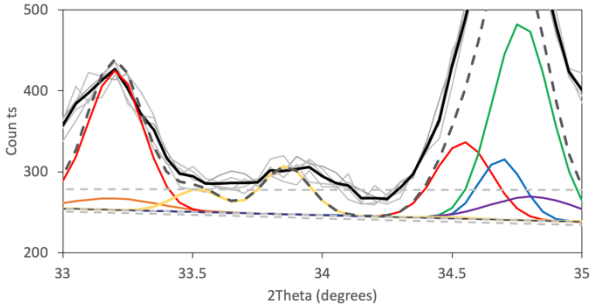

Figure 5: Comparison between the observed peak (major frames gray, average black), average background fits from different rounds of fitting (dashed), and the fit peak (gray, dashed) for jarosite. Peaks from individual minerals are shown: jarosite (yellow), feldspars (red, purple), pyroxenes (green, blue), cristobalite (orange).

Conclusions: A mineral specific determination of the LoD and LoQ of minor phases in mineral mixtures characteristic of Gale sedimentary rocks, using the CheMin instrument, is important ongoing work. We have determined the level of background scatter associated with a major frame and can now use that as a basis for determining LoD and LoQ. Results from Rietveld refinement of the CH diffraction pattern emphasize the importance of picking a good background fit, and in evaluating the uncertainty associated with overlapping peaks when determining if a minor phase is present above the LoQ.

References: [1] Blake D. et al. (2012) *Space Sci Rev, 170*, 341-399. [2] Treiman A.H. et al. (2016) *JGR: Planets, 121*, 75-106. [3] Rampe E. et al. (2018) *GRL, 45*, 9488-9497. [4] Achilles C. et al. (2017) *JGR: Planets, 122*, 2344-2361. [5] Bristow T.F. et al. (2018) *Sci adv, 4*, 3330. [6] Rampe E. et al. (2017) *EPSL, 471*, 172-185. [7] Morrison S.M. et al., (2018) MSA [8] Morrison S.M. et al. (2018) *Am Min: Jnl Earth & Plan. Mat., 103*, 857-871. [9] Cavanagh P. et al. (2015) *LPSC XLVI*.