LINEAR PROGRAMMING APPROACH TO QUANTITATIVE MINERALOGY ON MARS.

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Introduction: The Chemistry and Mineralogy (CheMin) instrument on the Mars Science Laboratory (MSL) is providing the first X-ray diffraction (XRD) data for rock and soil samples ever recorded on Mars [1, 4]. In addition to XRD, the Alpha Particle X-ray Spectrometer (APXS) provides a unique perspective into the chemostratigraphy of Mount Sharp [5]. In order to understand complex geologic samples that are composed of both crystalline and amorphous components, it is essential not only to measure the chemical composition of the whole sample, but also to quantify all individual components, both crystalline and disordered and/or amorphous. Current XRD analysis techniques, such as Rietveld refinement [6], provide quantitative crystalline mineralogy, but they have a limited capability to determine the abundance and composition of disordered and so-called X-ray amorphous materials, especially remotely on Mars. Due to the disordered nature of amorphous materials and many phyllosilicates, the Rietveld method is not suited to independently quantify all of the components in complex mixtures containing amorphous and/or clay mineral components.

As an extension of the XRD-determined mineralogy, more accurate models of the solids comprising each sample can be developed by considering different instrumental analyses of the same sample. Using linear programming methods with multiple data sets, previously shown to be effective at constraining quantitative mineralogy [7, 8], it is possible to clarify the abundances of amorphous and poorly ordered materials and further constrain the chemical variability of individual solid phases. Previous attempts to quantify both crystalline and non-crystalline components include mass balance [9, 10] and full-pattern fitting approaches [11].

Linear programming methods have been shown to be effective at optimizing particular variables in multi-component systems. We applied these methods to determine the maximum and minimum abundances of every phase in a complex mixture. The approach incorporates data for bulk composition from APXS and XRD-derived phase abundances from CheMin, as well as crystal structure, chemistry, and stoichiometry.

Methods: Each CheMin sample was broken down into individual components and represented as a system of equations relating various mineral constraints, phase variables, and a constant bulk composition vector. The empirical chemical formula of each phase, determined from stoichiometry and/or Rietveld refinement of unit-cell parameters, was used as the starting point for optimizing the abundance and composition of each phase.

Linear Programming Model. The goal of the linear programming problem is to maximize a particular phase, \( X_j \), while satisfying chemical mass balance equations. Each phase has an estimated abundance variability, defined as \( \Delta X_j \). For each phase, compositional variability was defined using literature data. The total mineral mixture is defined as the sum of multiple phases:

\[
X_j q'_j + 2[\Delta q] \Delta X_j,
\]

where \( q'_j \) is the starting composition and \( 2[\Delta q] \) is the compositional range of interest. The linear programming maximization is defined as:

\[
\text{Maximize } X_j + \sum (-100D) + \sum (-100D') \text{ subject to }
\]

\[
X[q'_j] + 2[\Delta q] \Delta X_j + \cdots + X[q'_n] + 2[\Delta q] X_j + D[ ] - D'[ ] + \cdots + D[n][ ] - D'[n][ ]
\]

with

\[
X_j \geq 0, \sum X_j = 1, X_j \geq (\Delta X)_j, 1 \leq i \leq n, 1 \leq j \leq m
\]

The number of phases in the mixture is defined as \( m \), and the total number of components needed to describe all of the phases is \( n \). Low-weighted free-variable \( D \) matrices are added to the objective function (the function being maximized) and the mass balance constraints in order to guarantee a solution. More information on the linear programming problem can be found in [8].

Computation. The Python package PuLP [12] was used to evaluate the linear programming model. The basic maximization problem is defined as:

\[
\text{Max } X_j \text{ such that }
A_{eq} x = B_{eq}
\]

\[
A x \leq B.
\]

The equality (\( A_{eq} \)) and inequality (\( A \)) are matrices, and (\( B_{eq} \), \( B \)), and (\( x \)) are vectors.

Rocknest Model. The Rocknest scoop 5 sample, the first sample analyzed by CheMin, represents global-scale aeolian mixing of Mars soil, with more-local contributions. Bish et al. [2] identified the four major mineral phases of the Rocknest soil as measured by CheMin: plagioclase (~An57), olivine (~Fo62), augite, and pigeonite. In addition, several minor phases were identified including magnetite, anhydrite, quartz, sanidine, hematite, and ilmenite. The bulk composition from the corresponding APXS analysis [1] was used in the model calculations.

Results: The maximization value was recorded for each iteration, and the minimum was determined by selecting the lowest value for a particular phase throughout all trials. The linear programming optimization for Rocknest scoop 5 produced the range of abundances shown in Table 1.

Discussion: In many cases, the optimization resulted in a phase maximum or minimum that was constrained by the limits of the model. The phases were allowed to vary within the ±2σ errors from [2]. Although this may not provide an improvement for particular crystalline phases, it does, however, provide a more narrow constraint on the abundance and chemical composition of the amorphous component.

Several methods have been used to estimate the crystalline and non-crystalline components of the samples analyzed by CheMin. Morris et al. [10] progressively subtracted the CheMin-identified phases in their respective abundances determined through Rietveld analysis, and they produced an approximation of the abundance and composition of the residual material. The chemical composition of the material remaining after this procedure includes a mixture of both the amorphous component(s) and any phyllosilicate components present in the sample. For the case of the Rocknest scoop sample, no phyllosilicate component was identified and hence the residual bulk composition should reflect the amorphous component and any trace minerals not identified by CheMin. The limitations of this method center around the inability of the mass balance method to account for variability within individual mineral compositions and the inability to differentiate between individual amorphous components. Alternatively, as presented here, by allowing the chemical composition of each phase to vary within realistic ranges, the model is able to better predict the nature of the soil mixture.

Conclusions: The results from the model of Rocknest scoop 5 sample indicate that the amorphous component is within a range of ~29-33 wt%. The result is consistent with the FULLPAT estimation of 27+/–15 wt%, although our result provides a narrower abundance range. Although comparable to the minimum estimation of 21-22 wt% from [9], our results more closely align with original estimates from the full-pattern fitting method. The results from [10] indicate 48.7 wt% amorphous, but the approach used did not account for potential chemical variability within individual phases.

The linear programming optimization procedure applied to the MSL XRD and APXS data shows that it is possible to determine approximate ranges of both crystalline and amorphous and/or disordered components of the samples analyzed by the CheMin instrument. Understanding the composition and proportion of the amorphous component(s) in Mars samples is essential to understanding the origin and role of amorphous components on early and modern Mars.

Acknowledgements: The authors acknowledge funding from NASA grant #NNX11AN36G. PDC was funded through both the Grassmann Fellowship for Clay Mineralogy and the Indiana Space Grant Consortium (INSGC) Doctoral Fellowship.

References: