REEVALUATION OF CHEMIN DATA: NEW CONSTRAINTS ON THE NATURE OF POORLY CRYSTALLINE MATERIALS ON MARS. N. C. Luu[1], E. M. Hausrath[1], E. Rampe[2], and T. S. Peretyazhko[3], [1]Department of Geoscience, UNLV Las Vegas, NV, USA (luun1@unlv.nevada.edu), [2]NASA Johnson Space Center, Houston, TX, USA, [3]Jacobs at NASA Johnson Space Center, Houston, TX, USA

Introduction: Full pattern fitting by FULLPAT [6] of X-ray diffraction (XRD) patterns collected by the Mars Science Laboratory (MSL) Curiosity's Chemistry and Mineralogy (CheMin) instrument demonstrated substantial amounts of X-ray amorphous and poorly crystalline component in all samples analyzed at Gale crater to date [1-7]. Chemical measurements indicate that these materials are Fe-rich (e.g. [1, 4, 11]), and measurements by the Sample Analysis at Mars (SAM) instrument indicate that at least some of them are likely weathering products based on their volatile contents (e.g. [8-10]).

However, despite their presence in the XRD patterns collected by Curiosity, and the importance of weathering products in understanding past environmental conditions on Mars, the components that make up the X-ray amorphous and poorly crystalline clay mineral fraction are not well-constrained. This is due in part to the limited database of FULLPAT software which is used to identify amorphous phases in CheMin XRD patterns. The database consists of seven X-ray amorphous patterns: two volcanic glasses, ferrihydrite, amorphous Fe(III)-silicate, opaline silica, allophane, and amorphous Mg-sulfate; and three clay patterns: one trioctahedral smectite and two dioctahedral smectites [1, 4]. To help further constrain the poorly crystalline materials on Mars, we are expanding the FULLPAT library with additional Mars-relevant X-ray amorphous and clay mineral materials. The database will be used to reanalyze the XRD patterns collected by MSL Curiosity which is crucial for understanding past environmental conditions on Mars.

Methods:

The FULLPAT program: FULLPAT is an Excel-coded application capable of quantifying the X-ray amorphous and poorly crystalline component, such as clay minerals, in an XRD pattern [6]. The X-ray amorphous component consists of broad diffraction peaks or a large "hump" in patterns, which are derived from materials that lack long-range crystallographic order [6, 12], while clay minerals display a broad (001) peak at low angles in a diffraction pattern. The publicly available version of FULLPAT contains a step size of 0.02 2θ and pattern range of 2-70° 2θ, and has been modified to fit the range for CheMin and TERRA (a field-portable CheMin-like diffractometer [19]), which extends from 5-50€2θ with a step size of 0.05 2θ.

Addition of materials to the FULLPAT library: Table 1 shows the minerals and amorphous materials that we are adding to the FULLPAT mineral library.

Table 1. Mars-relevant minerals and X-ray amorphous materials being added to the FULLPAT database.

Material	Unspiked	Spiked
Fe-rich allophane[1]	in prep	in prep
Ferrous saponite[2]	in prep	in prep
Ferric smectite[2]	X	X
100% Mg-bearing smectite[2]	X	X
5% Mg-bearing smectite[2]	X	in prep
15% Mg-bearing smectite[2]	X	in prep
50% Mg-bearing smectite[2]	X	in prep
Na-Montmorillonite (SWy-3) [3]	X	X
Beidellite (SBld-1)[3]	X	X
Hectorite (SHCa-1)[3]	X	X
Vermiculite[4]	in prep	in prep
Stevensite[5]	in prep	in prep

An "X" notation indicates that there is a sieved (< 150 μm) sample that has been run on TERRA. "In prep" indicates that it is either in the process of being synthesized, purchased, or being prepared for TERRA analysis. [1]synthesized after Ralston et al., in revision [13], [2]synthesized after Gainey et al., [14]; [3]purchased from the Clay Minerals Society (CMS); [4]purchasing from VWR; and [5]to be synthesized after Takahashi et al. [15].

Sample preparation: Samples (Table 1) are ground into a powder using an agate mortar and pestle and sieved through a 150 μm sieve. The < 150 μm powdered fraction is spiked with an internal standard of 20 wt. % corundum (Al_2O_3) to collect reference intensity ratios (RIRs) for all single phases that are being added to the FULLPAT library as well as mixtures that are being analyzed with FULLPAT.

Sample analysis on TERRA: Unspiked samples are being analyzed with TERRA, a portable charged coupled device (CCD) X-ray diffractometer equipped with a Co-kα X-ray tube. Mineral identification of unspiked samples is confirmed using X'Pert HighScore (Ver. 2.0a – 2.0.1). After sample identification and purity are confirmed, samples are spiked with 20 wt. % corundum, reanalyzed by TERRA, and RIRs are calculated. XRD patterns of unspiked samples along with their RIRs are loaded into the FULLPAT library.

CheMin analysis: CheMin and TERRA both operate in transmission geometry and utilize a Co-kα X-ray tube [16]. CheMin operates for about 8 hours a night and XRD data is acquired over multiple sols [4]. Data collected by the CheMin instrument are available to the

public on the Planetary Data System (PDS) [17] and the CheMin Open Data Repository [18].

Examination of the FULLPAT analysis: In order to examine uncertainty of the FULLPAT analysis, we made a mixture of equal proportions by weight (~33 wt. %) of ferric smectite, 50% Mg-bearing smectite, and 100% Mg-bearing smectite. We then spiked this mixture with 20 wt. % corundum, measured it on TERRA, and then analyzed the XRD pattern using FULLPAT for quantification of mineral phases.

Preliminary Results:

The version of FULLPAT modified to analyze patterns measured by TERRA was successful in fitting the unknown pattern to the minerals selected, correctly identifying the presence of each end-member smectite as well as the mixed Fe-Mg smectite (Figure 1). Although all three members of the mixture were correctly identified in concentrations of >19%, the concentrations measured by FULLPAT differed from the input measurements by ~10-25%. Additional work will be performed to test the identification and quantification of these additions to the FULLPAT database in mixtures relevant to Mars.

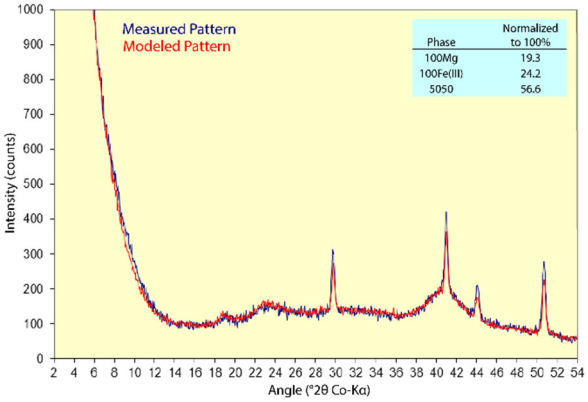

Figure 1. TERRA-measured XRD pattern of a mixture of equal amounts by weight of ferric smectite, 100% Mg-bearing smectite, and the 50% Mg-bearing smectite (in blue) and the FULLPAT modeled pattern (in red). FULLPAT correctly identified all three phases in abundances of at least 19%.

Conclusions and future work:

The remaining minerals from Table 1 that need to be added to the database will be measured on TERRA and added to the FULLPAT library. All Mars-relevant minerals and amorphous materials being added to the FULLPAT library will then be sent to NASA Johnson Space Center (JSC) for analysis on CheMin IV. We will then reanalyze all publicly available CheMin XRD patterns using the new database of phyllosilicates and amorphous materials. This work will allow additional constraints to be placed upon the characteristics of poorly crystalline and amorphous materials on Mars, with important implications for understanding past environmental conditions.

References:

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