

**X-RAY DIFFRACTION REFERENCE INTENSITY RATIOS OF AMORPHOUS AND POORLY CRYSTALLINE PHASES: IMPLICATIONS FOR CHEMIN ON THE MARS SCIENCE LABORATORY MISSION.** C. N. Achilles<sup>1</sup>, R. V. Morris<sup>2</sup>, S. J. Chipera<sup>3</sup>, D. W. Ming<sup>2</sup>, and E. B. Rampe<sup>2</sup> <sup>1</sup>ESCG/Hamilton Sundstrand, Houston, TX 77058, cherie.n.achilles@nasa.gov, <sup>2</sup>NASA Johnson Space Center, Houston, TX 77058, <sup>3</sup>Chesapeake Energy Corp., Oklahoma City, OK 73118,

**Introduction:** The CheMin instrument on the Mars Science Laboratory (MSL) rover Curiosity is an X-ray diffraction (XRD) and X-ray fluorescence (XRF) instrument capable of providing the mineralogical and chemical compositions of rocks and soils on the surface of Mars. CheMin uses a microfocus X-ray tube with a Co target, transmission geometry, and an energy-discriminating X-ray sensitive CCD to produce simultaneous 2-D XRD patterns and energy-dispersive X-ray histograms from powdered samples. Piezoelectric vibration of the cell is used to randomize the sample to reduce preferred orientation effects. Instrument details are provided in [1, 2, 3].

Analyses of rock and soil samples by the Mars Exploration Rovers (MER) show nanophase ferric oxide (npOx) is a significant component of the Martian global soil [4] and is thought to be one of the major contributing phases that the Curiosity rover will encounter if a soil sample is analyzed in Gale Crater. Because of the nature of this material, npOx will likely contribute to an X-ray amorphous or short-order component of a XRD pattern measured by the CheMin instrument.

Reference Intensity Ratios (RIR) are used to quantify minerals in mixed mineral systems using powder XRD analysis. Traditionally, RIR values are determined according to the following equation

$$\frac{I_i}{I_{std}} = k \frac{W_i}{W_{std}}$$

where  $I_i$  is the intensity of the analyte phase,  $I_{std}$  is the intensity of an internal standard phase,  $W_i$  is the weight fraction of the analyte phase,  $W_{std}$  is the weight fraction of the internal standard phase, and  $k$  is the reference intensity ratio [5]. That is, if the analyte phase (here the amorphous phase) and the standard phase are combined in 1:1 ratios, then the RIR value is determined by the intensity ratio between the two phases [5].

The objective of this study was to determine the RIR values for several candidate X-ray amorphous or short-order phases using a CheMin-like laboratory XRD instrument. Determining RIRs of X-ray amorphous and poorly crystalline materials will aid in the

quantitative analysis of Mars surface materials measured by the CheMin instrument on MSL.

**Materials and Methods:** CheMin IV instruments are laboratory versions of the CheMin flight unit and are used to baseline the capabilities of the flight instrument. Both natural and synthetic Martian analogs containing known X-ray amorphous phases were combined with a mineral standard (beryl) in approximately 1:1 weight ratios. Three X-ray amorphous phases were mixed with beryl: (1) GMS083011, synthetic basaltic glass having mean Gusev soil composition, (2) HWMK919 palagonite from Hawaii (< 5  $\mu$ m size fraction), and (3) DC03282008-HIB, a synthetic hisingerite. The mixtures were analyzed on the JSC CheMin IV instrument by summing 30 second exposures to obtain a pattern with ample intensity to background ratios. The RIR values of the amorphous phases were determined by measuring the area of the (100) beryl peak at 12.9° 2 $\theta$ , and the area under the amorphous scattering hump. For poorly crystalline phases such as hisingerite and palagonite, the area of the low-angle rise from 4-10° 2 $\theta$  is measured rather than the amorphous hump typically in the 20-40° 2 $\theta$  range. These phases show greater areas in the low rather than high angle region yielding a more accurate measurement and the ability to distinguish these phases from other true amorphous materials such as basaltic glass.

**Results:** CheMin IV patterns of the three analog materials are shown in Fig. 1. The broad amorphous hump in the middle regions of the pattern is shown in 1a while low-angle scattering is shown in 1b and 1c. RIR values for each sample are presented in Table 1.

Sample	Description	RIR
GMS083011	Basaltic glass	5.4
HWMK-919	Palagonitic tephra	5.9
DC03282008-HIB	Hisingerite	25.4

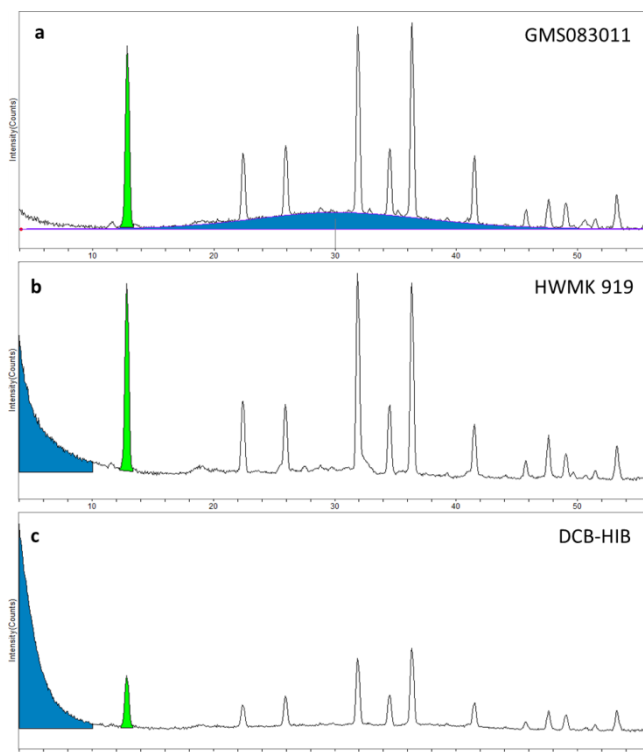
**Table 1** RIR values for measured amorphous and poorly crystalline phases.

**Implications for MSL:** Quantitative analysis of XRD patterns most often involves pure samples or mixtures of crystalline phases. However, analysis of martian analog samples along with data from previous and current Mars missions suggest the presence of poorly crystalline or X-ray amorphous materials. Characterizing these phases through profile fitting and RIR calculations allows for a more thorough analysis of data received from MSL's CheMin instrument. Although amorphous contributions in XRD patterns are often a contribution of many poorly crystalline phases, this data can be used to constrain models and provide more accurate quantities of predicted phases using full-pattern quantitative XRD methods [6].

These analyses can also aid in understanding the history of the sampled material. Results show that patterns which contain amorphous humps in the 15-35° 2 $\theta$  range are more likely to have a basaltic glass contribution whereas patterns showing a low-angle rise (4-10° 2 $\theta$ ) likely have a palagonite, or hisingerite contribution. In a companion study, Rampe et al. [7] observed similar behavior for allophane and ferrihydrite. Because glasses tend to be highly susceptible to aqueous alteration, the presence of this phase could indicate that the sample underwent little chemical weathering. Alternatively, presence of palagonite, hisingerite, and allophane would suggest opposite conditions (e.g. some aqueous weathering occurred).

MSL has just begun its prime mission on Mars. We anticipate that amorphous phases will be present in the Martian soil and aqueous altered rocks and outcrops encountered by Curiosity. The RIR values determined here will aid in identifying and quantifying X-ray amorphous and/or short-order phases by the MSL CheMin instrument.

**References:** [1] Blake D. F. et al, (2010) *LPSC XLI*, Abstract #1896. [2] Blake D. F. et al, (2009) *LPSC XL*, Abstract #1484. [3] Blake D. F. et al, (2007) *7<sup>th</sup> Int. Conf on Mars*, Abstract #3220. [4] Morris R. V. et al, (2008) *JGR*. [5] Snyder R. L. and Bish D. L. (1989) *Reviews in Mineralogy*. [6] Chipera S.J and Bish D.L. (2002) *J. Applied Crystallography*, 35, 744-749. [7] Rampe E.B. et al., (2013) *LPSC XLIV*.



**Figure 1** Beryl (green) and amorphous (blue) areas measured to calculate RIRs of each sample. (a) basaltic glass amorphous hump centered at 30° 2 $\theta$  (b) Low angle rise attributed to allophane (c) Low-angle rise attributed to hisingerite