TRANSMISSION ELECTRON MICROSCOPY ANALYSIS OF AMORPHOUS AND MICROCRYSTALLINE SILICATE MARTIAN ANALOGS TO BETTER UNDERSTAND MARTIAN AMORPHOUS MATERIALS

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Introduction: The Mars Science Laboratory (MSL) rover Curiosity has taken drill samples throughout its traverse of Gale crater. These samples have been analyzed by CheMin using X-Ray Diffraction (XRD). In every drill sample analyzed (**Fig. 1**), a large quantity of amorphous material has been identified that comprises anywhere between 15 to 70 wt% of the bedrock [1-4]. This amorphous material generally contains a large silicate component but may also contain other prominent components such as iron oxides and various sulfates [5].

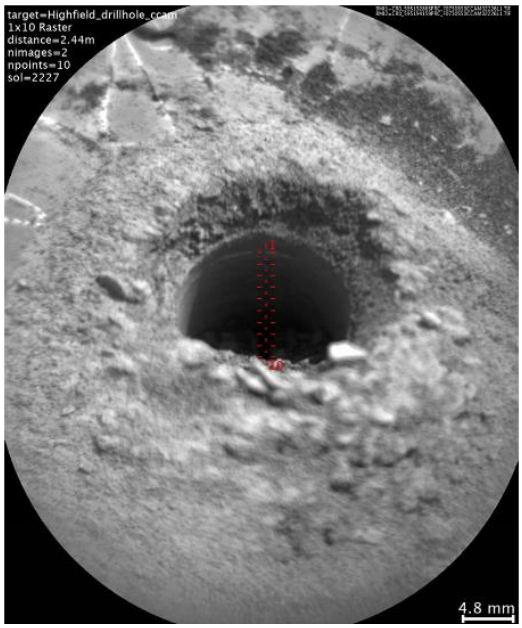

Fig. 1. Drill hole location Highfield where the amorphous component comprised nearly 50 wt% of the target.

ChemCam measures compositional abundances with Laser Induced Breakdown Spectroscopy (LIBS) producing spectra used to calculate wt% of oxides. While CheMin can estimate the fraction of the amorphous component, matrix effects from the abundance of amorphous materials can make it difficult for LIBS analysis to quantify the composition of the amorphous component. It is not well understood how amorphous materials affect the LIBS spectra and thus affect calculation of chemical abundances.

Amorphous phases have been identified in Mars Exploration Rover (MER) samples using Alpha Particle X-ray Spectrometer (APXS) and Miniature Thermal Emission Spectrometer (Mini-TES) methods as well as within martian meteorites [6,7]. Microcrystalline materials have also been detected in Gale Crater in the forms of opal and tridymite [8,9]. The reasons and environments that resulted in some material crystallizing while similar materials are amorphous remains poorly understood, calling for the need for terrestrial laboratory investigations.

Temperature, transformation kinetics and degree of hydration can all affect whether crystallization of amorphous materials occurs. Amorphous material, such as opal-A, can transform into crystalline material, such as opal-CT, if exposed to hydrothermal fluids between ~20 °C and ~60 °C [5]. The absence of opal-CT in some drill locations implies generally low-temperature diagenesis [5]. Amorphous iron oxides can result from hydrothermal alteration of magnetite [5]. The variability of abundance of amorphous iron oxides throughout the drill holes suggests multiple fluid events [3-5]. Lastly, amorphous sulfates may indicate a period of acidic conditions [5]. This poses an interesting dilemma as geochemical evidence suggests that Gale crater sediments experienced warm (up to 100 °C) temperatures to form clays, yet amorphous material still remains [10]. It is possible that the clays formed first and the amorphous material developed later, though this is still unknown. The wide variety of factors that may contribute to the formation of amorphous vs crystalline phases make the understanding of amorphous materials on Mars complicated, but of key importance in unravelling the diagenetic and alteration history of these materials.

Objective: The primary objectives of this study are to conduct analyses on Mars-relevant analog silicate samples using a combination of Transmission Electron Microscope (TEM) and XRD methods. These analyses will be used to understand the transition point between amorphous and microcrystalline materials and the factors that control the formation of both. Understanding of these factors may also help to determine if the amorphous material formed with the clays or after the clays had already formed.

Methods: The initial analyses will consist of amorphous Mg-silicate samples that are Mars-relevant in composition formed experimentally at the

University of Calgary [11]. The sample is formed by batch reactions involving silica from $Na_3SiO_3*9H_2O$ and magnesium from $MgCl_2$ using methods described in Che et al [12]. The resulting Mg-silicate, which is talc-like in composition, has been analyzed previously using FTIR, XRD, and Raman techniques, which have provided a general overview of the crystallinity and long-range ordering of the material [12]. These samples will be run using analytical TEM methods to get a fine scale understanding of their amorphous nature. Future analysis will include crystalline material of similar composition using the same methods used for the amorphous materials. A suite of amorphous and crystalline materials that range of formation conditions including temperature (from 0 to 100 °C), formation rate, and level of hydration (very dry to very hydrated) will be studied.

Sample preparation for TEM thin sections will use standard Focused Ion Beam (FIB) methods. These samples will then be characterized using a variety of TEM techniques, such as high resolution TEM imaging and high angle angular dark field imaging (HAADF). Selected area electron diffraction will be used for quantitative determination of the crystallinity [13,14]. Diffraction patterns obtained from the experimental materials can be used to calculate the d-spacings of minerals will be used to determine the degree of crystallinity of the materials at the submicron to nanometer scale. Energy dispersive x-ray spectroscopy (EDS) will be used to determine the composition of the material and electron energy loss spectroscopy (EELS) will be used to look at the bonding characteristics of Si and O, in materials with different degrees crystallinity from amorphous to fully crystalline. [13,15-17].

Results & Discussion: Results gathered from this study will facilitate an improved understanding of the fine scale structure of amorphous and microcrystalline materials relevant to Mars. Results will consist of quantitative analyses of amorphous and crystalline materials covering a range of formation conditions. These results will be compared with XRD analyses conducted on the same samples. This will allow comparison between TEM data, which provides analytical data at the micro to nanometer scale and XRD, which is a much larger volume bulk analysis method. These results can then be compared directly with Mars sample analyses taken by Curiosity and Perseverance.

Analysis will look at how temperature, formation rate, and hydration can influence the transformation of amorphous phases into crystalline phases or vice versa. This information will help constrain why some amorphous phases on Mars underwent crystallization while others have remained amorphous. Such data will help to further determine the initial formation conditions or diagenetic conditions present in Gale Crater that have resulted in the current lithology.

Analysis will include investigation of volcanic and diagenetic glasses and their interactions with magmatic and secondary waters, given the overall mafic compositions of martian materials [18,19]. Comparing between primary and secondary amorphous materials may help to determine if the amorphous material is detrital volcanic glass or if it formed later through diagenesis.

Conclusions and Future Work: TEM analysis of amorphous and crystalline silicate material may provide insight into the depositional and diagenetic conditions present in Gale crater. XRD techniques are currently the preeminent method for determining amorphous and crystalline phases. Incorporation of terrestrial TEM analyses on similar materials may be able to provide insight into poorly understood amorphous phases on Mars. Future work will include further TEM analysis of a wider variety of crystalline material and will also include XRD analysis for comparison with the TEM results.

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