

EXPLORING THE COMPOSITION AND NATURE OF THE X-RAY AMORPHOUS COMPONENTS OF MARTIAN SOIL AND ROCKS AT GALE CRATER, MARS. E. Dehouck¹, S. M. McLennan¹, P.-Y. Meslin², A. Cousin³, E. B. Rampe⁴, N. L. Lanza³, J. A. Hurowitz¹, W. Rapin², and the MSL science team. ¹Department of Geosciences, Stony Brook University, NY, USA (erwin.dehouck@stonybrook.edu); ²IRAP, UPS/CNRS/OMP, Toulouse, France; ³LANL, Los Alamos, NM, USA; ⁴NASA Johnson Space Center, Houston, TX, USA.

Introduction: Among the spacecrafts that have successfully landed on Mars, the Mars Science Laboratory rover Curiosity is the first equipped for X-ray diffraction (XRD) analysis, which is the most common method used on Earth to identify minerals in bulk geological samples. The diffractometer is part of the CheMin instrument [1], which receives <150- μ m powder samples from the sample collection and processing subsystem on the rover arm. During the first (terrestrial) year of the mission, CheMin analyzed samples from three locations: the Rocknest sand shadow (scooped) [2,3], and the John Klein (JK) and Cumberland (CB) outcrops (drilled) [4]. Both JK and CB are part of the Sheepbed mudstone, a rock unit in which CheMin XRD analyses have revealed the presence of smectite clay minerals [4]. Apart from the clay minerals, the Sheepbed mudstone shares some compositional characteristics with the Rocknest sand shadow: both contain a significant (>25 wt%) amorphous component in addition to several common basaltic minerals [2-4]. The process(es) that produced the amorphous material is (are) not yet established and could include: chemical weathering, rapid solidification of a volcanic or impact melt, modification of pre-existing phases induced by radiations or shock, etc. Here, we present the results of mass balance calculations that explore the domain of possible chemical compositions of the amorphous component within the Rocknest and CB samples. We also discuss the possible X-ray amorphous phases that could make up this amorphous material.

Methods: Following an approach similar to [5], we based our calculations on bulk chemical compositions measured by the APXS instrument, and on phase abundances and structural formulas derived from the CheMin XRD patterns by [2-4]. Using the Scilab software, we developed a program that allows calculation of all the possible chemical compositions of the crystalline component – and thus of the complementary amorphous component – of each sample, taking into account the uncertainties on the phase abundances derived from CheMin data [2,4]. For the Sheepbed mudstone, we chose to work only with the data from the CB drill in order to minimize the potential effect of cross-sample (i.e., Rocknest-JK) contamination [4].

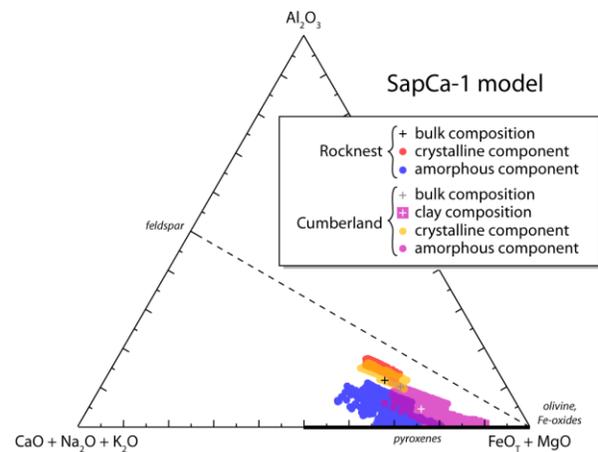
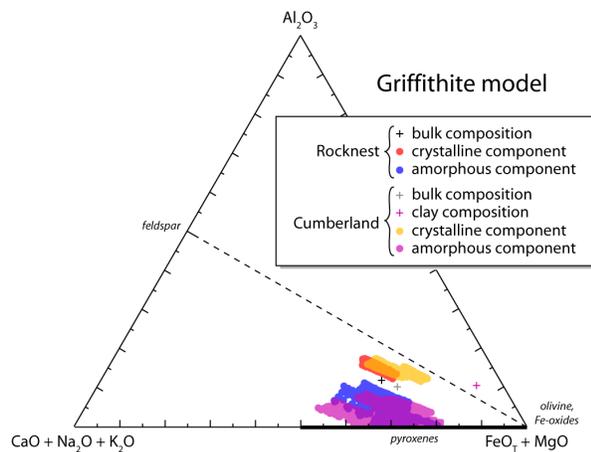
Chemistry: The calculated compositions are presented on A-CN-K-FM ternary diagrams (Fig. 1; A=Al₂O₃, CNK=CaO+Na₂O+K₂O, FM=FeO_T+MgO)

[6,7]. Two proportions of amorphous component are considered and plotted together in each case: 30 wt% (i.e., close to the XRD-based estimate) and 45 wt% (i.e., close to the chemistry-based estimate) [2-5]. In addition, because the exact nature of the smectite detected in the CB sample is unknown, we considered two possible endmembers [4]: griffithite, a Ca-poor, ferroan saponite; and Clay Minerals Society saponite SapCa-1, a Ca-rich, Fe-free saponite.

In most cases, on these diagrams, the chemical compositions of the crystalline component are clearly distinct from those of the amorphous component (the data points do not overlap, except for CB with the SapCa-1 model; Fig. 1). However, taken individually, most oxides do have some overlap in the case of CB (with the notable exception of Al₂O₃). This implies that combining data in ternary diagrams like those presented here may be a more effective method for identifying compositional trends (for example, in the ChemCam dataset) than looking at oxides individually. Nonetheless, for the Rocknest sample, the crystalline and amorphous components have distinct compositions for all major oxides except K₂O, which could allow for unique identification, if not mixed at a scale below the spot size of ChemCam.

The A-CN-K-FM diagrams also show that the ranges of possible compositions for the amorphous component of Rocknest and CB largely overlap each other (Fig. 1). This is true even if the two estimates of proportions of amorphous component (30 and 45 wt%) are considered separately (data not shown). Perhaps more importantly, this is true for the two types of smectites considered (griffithite and SapCa-1), despite their significantly different compositions (Ca-poor, Fe-rich vs Ca-rich, Fe-free). This implies that given the current uncertainties on the phase abundances derived from the XRD analyses, the amorphous components of the Rocknest and Sheepbed samples *may* have a similar chemical composition.

If the amorphous material is chemically similar in Rocknest and CB, this would imply that it did not significantly contribute to the formation of the smectite clays found in the Sheepbed mudstone [8]. This would be consistent with the estimated abundance of the amorphous component based on XRD patterns being very similar for the Rocknest, JK and CB samples (~30 wt%) [4], instead of being lower for JK and CB. An



alternative, but perhaps less likely explanation would be that the amorphous material of both samples has been involved in the aqueous processes that formed the smectites [8], and that the smectites have been later removed from the Rocknest sand by other processes (e.g., sedimentary segregation).

“Mineralogy”: Bish et al. [2] investigated the “mineralogical” composition of the amorphous component of Rocknest based on the CheMin data. They found that the XRD pattern was best fit by a Gusev-composition basaltic glass mixed with some allophane-like material. In Fig. 2, the calculated compositions of the amorphous component of Rocknest are plotted on a Si-Al-Fe ternary diagram. The data fall in a domain located roughly between a basaltic composition (the bulk Rocknest sample is basaltic) and hisingerite, an Fe-rich, Al-poor poorly-crystalline phase [9]. The relative proportion of glass and hisingerite would vary considerably (from <25 to >75 wt% of hisingerite) depending on the exact composition and proportion of the amorphous component (Fig. 2).

Conclusion and future work: Our calculations show that the amorphous materials of the Rocknest sand and Sheepbed mudstone may be more similar than previously thought [3,4]. They likely correspond to a mixture of basaltic glass and an Fe-rich, Al-poor “allophane-like” material, such as hisingerite. In future work, we plan to test the reactivity of such amorphous material using laboratory analogs.

References: [1] Blake D. et al. (2012) *Space Sci. Rev.*, 170, 341-399. [2] Bish D. L. et al. (2013) *Science*, 341, DOI: 10.1126/science.1238932. [3] Blake D. et al. (2013) *Science*, 341, DOI: 10.1126/science.1239505. [4] Vaniman D. et al. (2013) *Science*, DOI: 10.1126/science.1243480. [5] Morris R. V. et al. (2013) *LPSC XLIV*, abstract #1653. [6] Nesbitt H. W. and Wilson R. E. (1992), *Am. J. Sci.*, 292, 740-777. [7] McLennan S. M. et al. (2013) *Science*, DOI: 10.1126/science.1244734. [8] Bridges J. C. et al. (this conf.) *LPSC XLV*. [9] Eggleton R. A. (1987) *Clays Clay Min.*, 35, 29-37.

Figure 1 – Comparison of possible compositions of crystalline and amorphous components in Rocknest and Cumberland samples on A-CN-K-FM molar diagrams. Two proportions of amorphous component, 30 and 45 wt%, are considered and plotted together in each case. Two types of smectite compositions are also considered for Cumberland: griffithite (left) and SapCa-1 (right). See text for details. Overlapping data points are visible by transparency effects. These diagrams show only a subset of possible compositions calculated for Rocknest (>50,000 combinations) and Cumberland (>1 million), because the program adds a point to the diagram only if it is outside the range defined by the compositions already calculated.

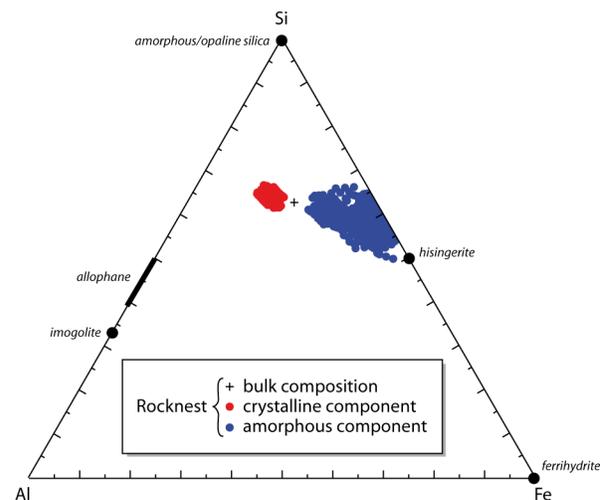


Figure 2 – Possible compositions of the crystalline and amorphous components of the Rocknest sample on a Si-Al-Fe molar diagram. Two proportions of amorphous components, 30 and 45 wt%, are considered and plotted together. Several poorly or noncrystalline secondary phases are also plotted [9].