CONSTRAINTS ON ABUNDANCES AND COMPOSITIONAL RANGES OF X-RAY AMORPHOUS COMPONENTS IN SOILS AND ROCKS AT GALE CRATER FROM MASS BALANCE CALCULATIONS.
E. Dehouck[1], S. M. McLennan[1], P.-Y. Meslin[2], A. Cousin[3], E. B. Rampe[4], R. V. Morris[4], N. L. Lanza[3], J. A. Hurowitz[1], W. Rapin[2], and the MSL science team. [1]Department of Geosciences, Stony Brook University, NY, USA (erwin.dehouck@stonybrook.edu); [2]IRAP, UPS/CNRS/OMP, Toulouse, France; [3]LANL, Los Alamos, NM, USA; [4]NASA Johnson Space Center, Houston, TX, USA.

Introduction: During the first (terrestrial) year of the Mars Science Laboratory mission, the CheMin X-ray diffraction instrument onboard the Curiosity rover [1] analyzed three samples: Rocknest – scooped from a sand shadow [2,3] –, and John Klein (JK) and Cumberland (CB) – drilled from rock [4]. Both JK and CB are part of the Sheepbed mudstone, which is the lowest exposed layer of the Yellowknife Bay formation [5]. The Sheepbed mudstone differs from the Rocknest soil mainly by the presence of smectite clays [4], but otherwise the two samples share a number of compositional characteristics: both contain a significant (~20-50 wt%) and yet-to-be-identified amorphous component in addition to several common basaltic minerals [2-4]. Determining or constraining the abundance and chemical composition of this major component of Martian soils and rocks (at least in the area explored by Curiosity) is an essential first step for understanding its origin, which in turn would be informative about the geological history of Gale crater, and of Mars in general [6]. 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.

Methods: Following an approach similar to [7], 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 [2-4]. We developed a program in Scilab that allows calculation of all the possible chemical compositions of the crystalline component – and thus of the complementary amorphous component – for each sample, taking into account the uncertainties in the phase abundances derived from CheMin data [2,4]. For the Sheepbed mudstone, we chose here to work only with the data from the CB drill hole in order to minimize the potential effects of cross-sample (i.e., Rocknest-JK) contamination [4].

In some cases, the calculated amorphous component may have one or more oxides with concentrations below 0 wt%: the combination is then rejected by the program. The lower the proportion of amorphous component, the more combinations are rejected. Thus, this constraint can be used to determine a lower limit to the overall abundance of the amorphous component, such that all oxides remain at or above 0 wt% (Fig. 1).

Results: The calculated compositional ranges of crystalline and amorphous components are shown in Table 1. The lower limits to the abundance of amorphous components are presented in Fig. 1.

Rocknest. The crystalline and amorphous components of the Rocknest soil have distinct compositions for all major oxides (including SiO_2, Al_2O_3, FeO_T, MgO, CaO and SO_3). This implies that it should be possible, at least theoretically, to distinguish the two components based on their distinct chemical composition, for example in the ChemCam dataset [8,9].

The lower limit on the abundance of amorphous component for Rocknest is 21 wt% (Fig. 1). In addition, proportions below 25 wt% can be considered as unlikely, because less than 5% of the calculated combinations are retained. These values are significantly higher than the lower limit (~14 wt%) and closer to the favored value (~27 wt%) estimated from the XRD pattern [2].

Cumberland. In the case of the Sheepbed mudstone, the exact nature of the smectite clay adds additional uncertainty on the estimate of the composition of the amorphous component. In accordance with [4], we used here two different smectite endmembers for our calculations: a Ca-poor, ferroan saponite from Griffith Park, CA (referred here as "griffithite"); and Clay Minerals Society saponite SapCa-1, a Ca-rich, Fe-free saponite (only the results for griffithite are reported in Table 1).

In contrast to Rocknest, crystalline and amorphous components of CB have overlapping ranges for most oxides (with the exception of Al_2O_3 for the griffithite model; Table 1), which means that chemistry alone may be insufficient to distinguish them. However, evaluating data on ternary diagrams (e.g., A-CNK-FM [10]) may be one way to avoid this issue [11].

The lower limit on the abundance of the amorphous component of CB is 16 wt% with smectite as griffithite and 12 wt% with smectite as SapCa-1 (Fig. 1). Proportions below 22 wt% and 18 wt% are unlikely (less than 5% of combinations are retained). These values are slightly higher than the lower limit estimated from the XRD pattern (~12 wt%) [4].

Comparison between Rocknest and Cumberland. From Table 1, the main difference between the amorphous component of the Rocknest soil and the CB

mudstone is the SO_3 content (~10 to 17 wt% vs <1 to ~7 wt%, respectively). This reflects both the higher S content of the bulk sample (5.45 vs 2.57 wt%) measured by APXS and the lower amount of S-bearing crystalline phases detected by CheMin [4]. (However, note that JK drill fines have SO_3 content of 5.61 wt%, closer to Rocknest than CB.) Since sulfur can originate either directly from the source rocks of the sediments or from later interactions with fluids [10,12], the above values do not necessarily imply a different origin for the amorphous components of Rocknest and CB.

Apart from sulfur, and given current uncertainties on phase abundances derived from CheMin data, the amorphous components of the Rocknest and Sheepbed samples have similar compositional ranges for all major oxides [11]. In particular, both have very low Mg and Al contents, possibly approaching 0 wt% (Table 1).

Conclusion: Our mass balance calculations allowed us to explore the domain of possible compositions of the amorphous components detected in the Rocknest soil and the Sheepbed mudstone by Curiosity. The results show that they may be chemically similar, except for the SO_3 content. Any formation hypothesis will have to account for these similarities and differences. Lastly, our calculations provide an independent way to determine lower limits on the abundances of the amorphous components within the bulk samples.

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. (2014) *Science*, *341*, DOI: 10.1126/science.1239505. [4] Vaniman D. et al. (2014) *Science*, *343*, DOI: 10.1126/science.1243480. [5] Grotzinger J. et al. (2014) *Science*, *343*, DOI: 10.1126/science.1242777. [6] Rampe E. B. et al. (2014) *this conf.* [7] Morris R. V. et al. (2013) *LPSC XLIV*, abstract #1653. [8] Fisk M. et al. (2014) *LPSC XLV*, abstract #1674. [9] Blaney D. et al. (2014) *LPSC XLV*, abstract #2122. [10] McLennan S. M. et al. (2014) *Science*, *343*, DOI: 10.1126/science.1244734 [11] Dehouck E. et al. (2014) *LPSC XLV*, abstract #1454. [12] Nachon M. et al. (2014) *LPSC XLV*, abstract #2006.

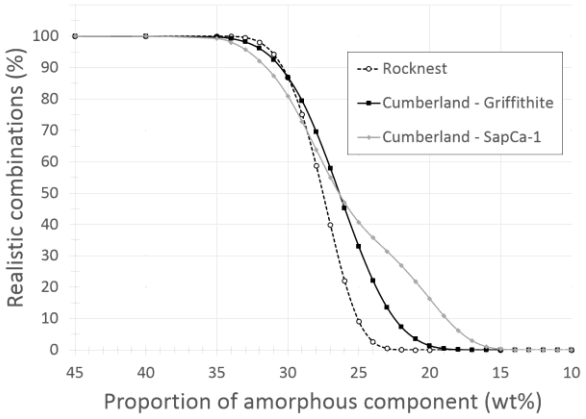

Figure 1 – Percentage of realistic combinations (i.e., compositions with all oxides >0 wt%) as a function of the proportion of amorphous component in the bulk sample. Starting below ~35 wt% of amorphous component, more and more combinations (and ultimately, all of them) are rejected because of MgO and/or Al_2O_3 contents below 0 wt%. Total number of combinations is 59,049 for Rocknest and 1,417,176 for Cumberland.

	Rocknest			***Cumberland ("griffithite")***		
	Crystalline component[a]	**Amorphous component**		**Crystalline component[a]**	**Amorphous**	
		30 wt%	**45 wt%**		**30 wt%**	**45 wt%**
SiO_2	44.3—49.8	26.7—39.6	34.4—41.2	40.6—48.2	30.9—48.7	36.7—46.0
TiO_2	0.1—1.2	1.3—3.8	1.2—2.6	0.1—0.8	1.7—2.9	1.2—2.0
Al_2O_3	10.8—14.5	0.0—6.3	3.2—7.8	10.1—14.0	0.0—5.0	2.0—6.7
FeO_T	12.7—18.0	21.9—34.0	20.6—27.1	18.1—25.5	15.0—32.2	18.5—27.5
MgO	10.2—13.3	0.0—5.2	3.0—6.9	7.1—12.4	2.5—14.7	5.8—12.3
CaO	7.5—10.0	0.9—6.7	3.9—7.0	4.8—7.9	3.5—9.8	4.3—8.2
Na_2O	1.8—2.4	3.8—5.0	3.1—3.9	1.6—3.0	3.8—6.1	3.0—4.6
K_2O	0.1—0.6	0.3—1.5	0.4—1.0	0.2—0.7	0.4—1.1	0.3—0.8
SO_3	0.4—1.5	14.7—17.2	10.3—11.6	0.9—4.0	0.4—6.5	0.8—4.6

Table 1 – Calculated compositional ranges of crystalline and amorphous components in Rocknest (left) and Cumberland (right; griffithite model only). Two proportions of amorphous component, 30 and 45 wt%, are considered in each case. Gray cells indicate where ranges for crystalline and amorphous components overlap. [a]Range shown for crystalline component is for 45 wt% of amorphous component, i.e., with no combination rejected.