

INDEPENDENT CHARACTERIZATION OF THE AMORPHOUS COMPONENT OF MARTIAN SOILS USING CHEMCAM LIBS DATA. E. Dehouck¹, G. David², P.-Y. Meslin², A. Cousin², O. Gasnault², O. Forni², S. Maurice², R. C. Wiens³. ¹Laboratoire de Géologie de Lyon – Terre, Planètes, Environnement (LGL-TPE), Université de Lyon, France (erwin.dehouck@univ-lyon1.fr), ²Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse, France, ³Los Alamos National Laboratory (LANL), Los Alamos, NM, USA.

Introduction: Ever since the first *in situ* missions to Mars, the mineralogy of Martian soils has been a subject of great interest. Because they were unable to move, the *Viking* landers mostly analyzed the soils around them. Early interpretations, based on X-ray fluorescence results and spectral comparisons with Earth analogs, favored a mineralogical composition dominated by secondary phases such as smectites, kieserite and calcite [e.g., 1]. Years later, Mössbauer measurements carried out by the *Spirit* and *Opportunity* rovers provided the first direct constraints on the mineralogy of Martian soils, although restricted to Fe-bearing phases. They revealed the presence of olivine, pyroxenes, magnetite and nanophase ferric oxides [2]. More recently, soon after its arrival on Mars, the *Curiosity* rover carried out a detailed characterization of a sand shadow named Rocknest, which still serves as the reference soil for Gale crater. In particular, the CheMin X-ray diffractometer was able to identify and quantify all crystalline phases above its detection limit of ~1 wt% [3-6]. However, the CheMin analysis also revealed the presence of a significant X-ray amorphous component (35 ± 15 wt%), which appears to be enriched in volatiles, since the crystalline phases cannot account for the hydrogen and sulfur contents measured by the SAM, ChemCam and APXS instruments [4, 7, 8]. Thus, the amorphous component (hereafter abbreviated as “AmC”) could represent an important marker of past aqueous alteration processes.

Previous efforts to characterize the nature and origin of the AmC of the Rocknest sample have focused on mass balance calculations, which consist of subtracting from the bulk composition of the soil the composition of each crystalline phase, in proportion to its abundance [e.g., 4, 9]. This method provides first-order constraints on the composition of the AmC for major elements, but suffers from quite large uncertainties and could be strongly biased for low-abundance elements due to undetected crystalline phases [9]. Here, we propose to use ChemCam LIBS (laser-induced breakdown spectroscopy) data to independently confirm and refine the composition of the AmC of Martian soils, and to gain access to its content in minor and trace elements.

Data and methods: For the purpose of this study, we produced new estimates of the composition of the AmC of the Rocknest soil (**Table 1**), following the mass balance approach described in [9]. These calculations are based on the bulk chemical composition measured by the APXS instrument (Portage disturbed soil) – modified to include

2 wt% H₂O [7] – and on recently updated mineralogical information derived from CheMin XRD data [5, 6].

We then compared the mineralogy of the Rocknest sample to elemental compositions measured by the ChemCam instrument (**Fig. 1**). To this end, we selected 14 soil analyses (comprising between 5 and 10 individual LIBS points, with each point corresponding to 30 or 50 consecutive laser shots) performed during the first 100 sols of the mission, i.e., in the same region as Rocknest. Because CheMin analyzed a sieved sample of soil, we removed from our ChemCam dataset the contribution of coarse grains – larger than the laser beam, i.e., larger than ~350-500 μm – that were identified based on shot-to-shot variations of the total emission intensity [10]. We also removed the contribution of recently-deposited airborne dust by ignoring the first 3 shots of each LIBS point. After applying these filters, 1208 single-shot analyses remained, for which the composition in major oxides was determined using the quantification procedure described in [11].

Oxide (wt%)	Best-case ^a	Full range ^b
SiO ₂	32.2	19.8–37.9
TiO ₂	2.1	1.4–4.2
Al ₂ O ₃	5.1	0.0–7.6
Cr ₂ O ₃	<i>1.4</i>	<i>1.0–2.4</i>
FeO _T	20.2	18.1–25.1
MnO	<i>1.2</i>	<i>0.8–2.1</i>
MgO	4.4	0.0–6.8
CaO	5.6	2.4–6.8
Na ₂ O	3.1	2.8–3.9
K ₂ O	1.4	1.0–2.4
P ₂ O ₅	2.7	1.9–4.7
SO ₃	<i>13.8</i>	<i>9.7–24.3</i>
Cl	<i>1.9</i>	<i>1.4–3.4</i>
H ₂ O ^c	5.7	4.0–10.0
CCAM missing ^d	26.7	18.7–46.9

Table 1 – Composition of the AmC of Rocknest, estimated by mass balance calculations using the APXS bulk chemical composition (Portage) and recently updated CheMin mineralogy [5, 6].

^aThe best-case calculation assumes 35 wt% of AmC and no uncertainties in mineral abundances. ^bThe full compositional range is calculated using the method of [9], taking into account uncertainties in the abundances of the crystalline phases and in the abundance of the amorphous component itself (i.e., 35 ± 15 wt%), both reported in [5]. ^c2 wt% H₂O measured by SAM [7] was added to the APXS composition. ^dSum of the oxides/elements reported in italic, which are not currently quantified by ChemCam.

Results: Overall, the ChemCam single-shot analyses shown in Figure 1 appear to be in good agreement with the mineralogy of the Rocknest sample derived from CheMin data. In particular, the point cloud largely overlaps with the composition of the crystalline component, i.e., the weighted average of all crystalline phases (red-outlined square). From there, two mixing lines can be identified. The first one goes toward the plagioclase composition (green circle), whereas the second one goes toward the composition of the AmC (red-outlined circle). Based on laboratory analogs [12], for mechanical mixtures of grains smaller than the laser beam, such mixing trends are only expected to appear for components present at a level of several tens of wt%, which is consistent with the abundance of plagioclase and AmC estimated from CheMin data (~26 wt% and ~35 wt% of the bulk sample, respectively) [5]. Alternatively, coarser grains or coatings could also favor the appearance of such trends [12]. On the other hand, there is no obvious mixing trend toward olivine (purple), augite (light blue) and pigeonite (dark blue), which might be explained by their lower abundance (~13 wt%, ~12 wt% and ~8 wt%, respectively) [5] and/or by a smaller grain size.

The mixing trends observed in the ChemCam dataset confirm two distinctive characteristics of the AmC: it is depleted in Si and Al, and enriched in Fe (Table 1) compared to the crystalline component. The trends for MgO and CaO are less clear, but do not seem to contradict the results of the mass balance. In contrast, the trends for TiO₂, Na₂O and K₂O (not shown) suggest that these oxides are overestimated by the mass balance approach.

Of particular interest is the plot showing the sum of oxides vs SiO₂. In ChemCam analyses, the sum of oxides is not forced to 100 wt%, and therefore reflects the presence of not-quantified elements, among which are important volatile species such as H, S and Cl. On this plot, the agreement between the ChemCam point cloud and the estimated AmC composition is remarkable and further confirms that the amorphous component is the bearer of the volatiles in Gale soils.

Conclusion and future work: The ChemCam single-shot analyses of fine-grained soil targets reveal mixing trends toward two major components identified by CheMin at Rocknest, namely plagioclase and the AmC. The latter is confirmed to be depleted in Si and Al, and enriched in Fe and volatiles compared to the crystalline component. Discrepancies are observed for less-abundant elements such as Ti, Na and K, for which the mass balance approach is expected to be less reliable. Finally, this work opens the possibility of estimating which trace elements are associated with the AmC, which may help to better understand its origin.

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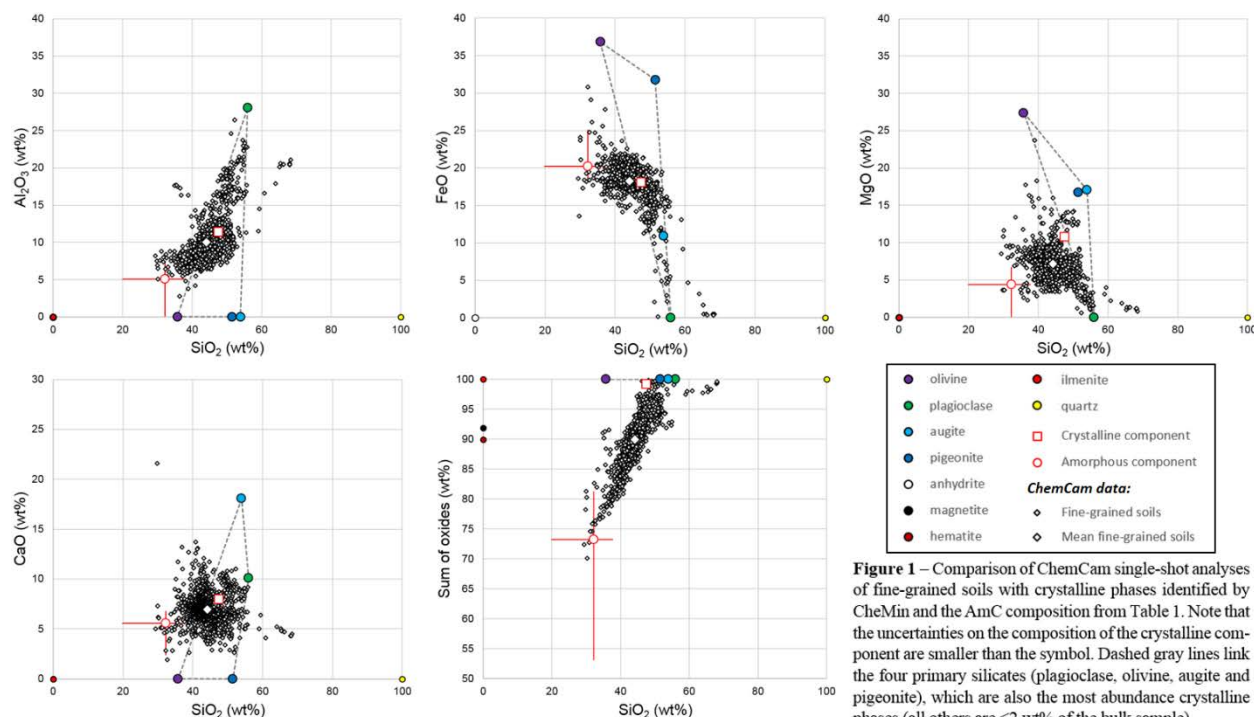


Figure 1 – Comparison of ChemCam single-shot analyses of fine-grained soils with crystalline phases identified by CheMin and the AmC composition from Table 1. Note that the uncertainties on the composition of the crystalline component are smaller than the symbol. Dashed gray lines link the four primary silicates (plagioclase, olivine, augite and pigeonite), which are also the most abundance crystalline phases (all others are <2 wt% of the bulk sample).