UPDATE ON THE CHEMICAL COMPOSITION OF CRYSTALLINE, SMECTITE, AND AMORPHOUS COMPONENTS FOR ROCKNEST SOIL AND JOHN KLEIN AND CUMBERLAND MUDSTONE DRILL FINES AT GALE CRATER, MARS.

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Background: We have previously calculated the chemical compositions of the X-ray-diffraction (XRD) amorphous component of three solid samples (Rocknest (RN) soil, John Klein (JK) drill fines, and Cumberland (CB) drill fines) using major-element chemistry (APXS), volatile-element chemistry (SAM), and crystalline-phase mineralogy (CheMin) obtained by the Curiosity rover as a part of the ongoing Mars Science Laboratory mission in Gale Crater [1,2]. According to CheMin analysis, the RN and the JK and CB samples are mineralogically distinct in that RN has no detectable clay minerals and both JK and CB have significant concentrations of high-Fe saponite [3,4,5]. The chemical composition of the XRD amorphous component is the composition remaining after mathematical removal of the compositions of crystalline components, including phyllosilicates if present [1,2,6].

Subsequent to [1,2,6], we have improved the unit cell parameters for Fe-forsterite, augite, and pigeonite, resulting in revised chemical compositions for the XRD-derived crystalline component (excluding clay minerals) [7]. We update here the calculated compositions of amorphous components using these revised mineral compositions.

Chemical Composition Calculations: The CheMin data are used to constrain the relative abundance of all crystalline phases and the chemical composition of crystalline phases whose unit cell parameters are sufficiently constrained to permit calculation of derived compositions (e.g., Fe-forsterite, augite, and pigeonite). For other crystalline phases, chemical compositions are assigned either by stoichiometry (e.g., hematite, basanite, and anhydrite) or by chemical compositions derived from Mars meteorites (e.g., orthopyroxene). Because the CheMin unit cell parameters are not sensitive to minor substitution (e.g., Cr, Mn, and Ti in pyroxene and Ni and Cr in olivine), we have supplemented the CheMin-derived chemical compositions with chemical data for those elements from Mars-meteorites for mineralogically-equivalent phases [8]. Data from SAM were used to provide abundances for total H_2O and CO_2 [9]. SAM, APXS, CheMin data for SO_3 and Cl abundances must be mutually consistent, with total SO_3 and Cl constrained by APXS values.

SAM data [9] were used to constrain the saponite abundance in JK and CB (20 wt.%) with the chemical composition of a terrestrial ferrian saponite that matched the 02ℓ diffraction band for JK and CB saponite [5,10]. Other smectite minerals (low-Fe saponite, nontronite, and montmorillionite) are not acceptable on this basis.

Bulk chemical composition: The bulk chemical compositions (APXS and SAM data) and the calculated chemical compositions for the XRD crystalline and XRD amorphous components are summarized in Table 1. Multiple entries for an oxide/element are listed when independent constraints that distinguish among oxidation states are available from CheMin. For example, Fe-CHMN, FeO-CHMN, and Fe_2O_3-CHMN are listed to accommodate Fe in pyrite and pyrrhotite, Fe^{2+} in olivine and pyroxene, and Fe^{3+} in hematite and akaganeite, respectively. Residual Fe is entered into the FeO+Fe_2O_3-UnAssign row. Similarly, S-CHMN, SO_3-CHMN, SO_3-SAM, and SO_3-UnAssign are listed to accommodate S in pyrite and pyrrhotite, SO_3 in Ca-sulfates, SO_3 in SAM-detected sulfates, and unassigned sulfates. Total Cl (measured by APXS) is partitioned into the concentration of Cl detected by SAM as perchlorate (Cl_2O_7-SAM) and the remaining Cl concentration (Cl-UnAssign). Total H_2O (measured by SAM) is partitioned into H_2O from crystalline phases (H_2O-CHMN; basanite and akaganeite) with the remaining H_2O concentration (including OH associated with Fe-saponite) listed on the H_2O row.

XRD crystalline component chemical composition. The XRD crystalline components (excluding smectite) for RN, JK, and CB are primary igneous minerals with minor amounts of secondary phases (e.g., anhydrite, bassanite, and akaganeite) and comprise 51 wt.%, 37 wt.%, and 41 wt.% of the bulk chemical composition, respectively (Table 1). The RN crystalline component is anhydrous within detection limits. JK and CB have Fe-saponite, basanite, and akaganeite as H_2O/OH-bearing phases. The most significant change in the composition of the crystalline component compared to previous calculations resulted from the revision of the of the Fe-forsterite composition from ~Fo60 to ~Fo40.

Smectite chemical composition: We used the chemical composition of ferrian saponite [10] for the smectite identified in JK and CB. Also, we assumed significant interlayer water was not present based on the collapsed nature of the CheMin JK and CB patterns

XRD amorphous component chemical composition: The XRD amorphous component comprises 49, 43, and 39 wt.% of bulk sample for RN, JK, and CB, respectively (Table 1). The nature and number of XRD amorphous phases that constitute the amorphous component is not unequivocally known, and there can be contributions from crystalline or other components if they do not coherently diffract X-rays.

The chemical compositions of RN, JK, and CB amorphous components (including volatiles) are broadly similar in the sense that they, compared to the crystalline components, have low SiO_2 and Al_2O_3 concentrations with $SiO_2/Al_2O_3>6$ and high $\sum(Fe+FeO+Fe_2O_3)$ and $\sum(S+SO_3)$ concentrations. Compared to [1,2,6], the revised $(\sum(Fe+FeO+Fe_2O_3))/MgO$ ratio for the RN amorphous component (~2) is significantly lower than previously calculated (~5) with~45 wt.% amorphous component. These element concentrations and ratios and volatile inventory show that the amorphous component is not a primary basaltic glass, although such a glass was a surrogate to model the concentration of the XRD-derived amorphous component for RN [3]. The high SO_3 concentration of all 3 amorphous components implies the presence of amorphous S-bearing phases.

References: [1] Morris et al. (2013) *LPSC44*, abstract #1653. [2] Morris et al. (2014) *LPSC45*, abstract #1319. [3] Bish et al. (2013) *341*, DOI:10.1126/science.1238932. [4] Blake et al. (2013) *Science*, *341*, DOI:10.1126/science.1239505. [5] Vaniman et al., (2013) *Science*, DOI:10.1126/ science.1243480. [6] Dehouck et al. (2014) *JGR*, *119*, DOI: 10.1002/2014JE004716. [7] Morrison et al. (2015) *LPSC46*, this volume. [8] Papike *et al.* (2009) *GCA*, *73*, 7443. [9] Ming *et al.* (2014) *Science*, 343, DOI: 10.1126/science.1245267. [10] Treiman *et al.* (2014) *Am. Min.*, *99*, 2234.

Table 1. Chemical composition of bulk sample, XRD crystalline (except saponite), ferrian saponite, and XRD amorphous components based on APXS, CheMin, and SAM datasets for RN soil and JK and CB drill fines.

	Bulk			XRD Crystalline			Saponite	XRD Amorphous		
Element (wt.%)	RN	JK	CB	RN	JK	CB	JK & CB	RN	JK	CB
SiO_2	41.18	40.54	40.58	46.21	41.64	43.46	45.83	35.88	37.10	34.85
TiO_2	1.14	0.97	0.98	0.94	1.55	2.49	0.28	1.36	0.79	-0.25
Al_2O_3	8.98	8.29	8.49	12.26	13.78	13.04	9.57	5.52	2.99	3.16
Cr_2O_3	0.47	0.42	0.42	0.23	0.41	0.52	0.01	0.72	0.61	0.53
FeO+Fe_2O_3-UnAssign	2.80	13.27	12.93	-0.04	-0.15	-0.12	16.49	5.77	23.24	24.80
Fe-CHMN	0.00	0.57	0.50	0.00	1.54	1.22	0.05	0.00	0.02	0.00
FeO-CHMN	9.08	3.66	4.95	17.71	9.55	12.09	0.00	0.00	0.00	0.00
Fe_2O_3-CHMN	1.00	1.32	1.73	1.88	3.60	4.22	0.00	0.07	-0.02	0.00
Fe_2O_3-npOx	6.42	0.63	1.01	-0.07	1.75	2.45	0.00	13.26	-0.03	0.00
MnO	0.39	0.25	0.29	0.29	0.16	0.20	0.39	0.51	0.26	0.35
MgO	8.33	8.81	9.05	8.04	6.00	6.83	17.02	8.64	7.34	7.27
CaO	6.96	7.55	6.39	9.18	10.72	8.25	4.22	4.62	6.39	5.54
Na_2O	2.59	2.88	2.88	2.22	2.47	2.31	0.76	2.97	4.23	4.58
Na	0.00	0.02	0.06	0.00	0.07	0.14	0.00	0.00	-0.02	0.00
K_2O	0.47	0.55	0.63	0.21	0.36	0.49	0.09	0.74	0.92	1.06
P_2O_5	0.90	0.93	0.89	-0.01	-0.01	-0.01	0.03	1.86	2.16	2.28
SO_3-UnAssign	1.78	3.14	3.44	-0.02	-0.03	-0.03	0.15	3.68	7.29	8.80
S-CHMN	0.00	0.37	0.30	0.00	1.07	0.74	0.00	0.00	-0.06	0.00
SO_3-CHMN	0.46	1.56	0.27	0.89	4.19	0.67	0.00	0.00	0.04	-0.01
SO_3-SAM	3.00	0.35	0.20	-0.03	0.00	0.00	0.01	6.19	0.81	0.50
Cl-UnAssign	0.51	0.63	1.05	-0.01	0.24	0.40	0.03	1.06	1.24	2.25
Cl_2O_7-SAM	0.39	0.12	0.41	0.00	0.00	0.00	0.02	0.81	0.27	1.05
H_2O	2.00	2.04	1.90	-0.02	-0.02	-0.02	4.79	4.14	2.50	2.44
H_2O-CHMN	0.00	0.12	0.14	0.00	0.38	0.43	0.00	0.00	0.00	-0.10
CO_2-SAM	1.00	0.70	0.25	-0.01	-0.01	0.00	0.00	2.06	1.63	0.65
Sum	99.85	99.68	99.74	99.85	99.68	99.74	99.76	99.85	99.68	99.74
$\sum(Fe+FeO+Fe_2O_3)$	19.30	19.46	21.11	19.49	16.70	19.85	16.54	19.89	23.21	24.80
$\sum(SO_3)$	5.24	5.42	4.21	0.84	5.23	1.37	0.16	9.88	8.09	9.30
Whole Sample	100.0	100.0	100.0	51.3	36.8	41.0	20.0	48.7	43.0	38.9

Notes: CHMN=CheMin; SAM=Sample Analysis at Mars. CheMin data from [3-5,9], and SAM data from [9]. For JK and CB, the smectite is interpreted as ferrian saponite with chemistry from [10] without interlayer H_2O. Ferrian saponite abundance for JK and CB (20 wt.%) is from [9].