CHEMICAL COMPOSITION OF CRYSTALLINE, SMECTITE, AND AMORPHOUS COMPONENTS FOR ROCKNEST SOIL AND JOHN KLEIN AND CUMBERLAND MUDSTONE DRILL FINES USING APXS, CHEMIN, AND SAM DATASETS FROM GALE CRATER, MARS. R.V. Morris[1], D.W. Ming[1], R. Gellert[2], D.T. Vaniman[3], D.L. Bish[4], D.F. Blake[5], S.J. Chipera[6], R.T. Downs[7], A.H. Treiman[8], A.S. Yen[9], C.N. Achilles[4], P.D. Archer[1], T.F. Bristow[5], J.A. Crisp[9], D.J. Des Marais[5], J.D. Farmer[10], J.P. Grotzinger[11], P.R. Mahaffy[12], A.C. McAdam[12], J.M. Morookian[9], S.M. Morrison[7], E.B. Rampe[1], and the MSL Science Team. [1]NASA JSC (richard.v.morris@nasa.gov), [2]UofGuelph, [3]PSI, [4]IndianaU, [5]NASA ARC, [6]CHK Energy, [7]UofA, [8]LPI, [9]JPL/Caltech, [10]ASU, [11]Caltech, [12]NASA GSFC.

Introduction: Three solid samples have been analyzed for major-element chemistry (APXS), volatiles (SAM), and crystalline-phase mineralogy (CheMin) by the Curiosity rover as a part of the ongoing Mars Science Laboratory mission. Rocknest (RN) soil was obtained from a sand shadow and is considered to be chemically and mineralogically equivalent to other basaltic soils analyzed as a part of Mars Exploration Mission (MER) Mission [e.g., 1]. APXS analyzed disturbed bulk soil on the martian surface, and CheMin and SAM analyzed the <0.150 mm size fraction of scooped soil. John Klein (JK) and Cumberland (CB) fines were obtained by drilling into mudstone at Yellowknife Bay in two locations ~3 m part. APXS analyzed drill fines located on the surface, and CheMin and SAM analyzed the <0.150 mm size fraction of scooped drill fines. According to CheMin analysis, the RN and the JK and CB samples are distinctly different mineralogically in that RN has no detectable clay minerals and JK and CB have significant clay minerals (tri-octahedral smectite) [2,3].

Chemical Composition Calculations: The calculated chemical compositions of the XRD crystalline and XRD amorphous components merging data from APXS, CheMin, and SAM [1,3,4] are summarized in Table 1. These calculations supersede those published previously [1,3] because they include volatile inventories from SAM. For the smectite component of JK and CB we used the chemical composition of griffithite, a high-Fe tri-octahedral smectite whose 02ℓ peak position corresponds to that for JK and CB [3,5]. Other smectites (low-Fe saponite, nontronite, and montmorillionite) are less viable interpretations on this basis.

Bulk chemical composition. The bulk chemical compositions are the APXS oxide/element plus SAM volatile (H_2O and CO_2) concentrations, including partitioning according to CheMin and SAM constraints are listed in Table 1. The SO_3 concentration is the APXS SO_3 concentration minus the SAM-measured SO_3 (SO_3-SAM) and the equivalent S concentration measured by CheMin (S-CHMN; phyrrhotite). The total Fe concentration as FeO from APXS was partitioned into FeO-CHMN, Fe_2O_3-CHMN, and Fe-CHMN according to Fe^{2+}- Fe^{3+}-, and Fe-bearing phases, respectively, from CheMin. The remaining FeO is listed as FeO+Fe_2O_3. The H_2O concentration is the SAM-measured H_2O concentration minus the H_2O in XRD crystalline phases (H_2O-CHMN; bassanite). The listed Cl concentration is the APXS concentration minus the Cl from the SAM-measured perchlorate (Cl_2O_7) concentration.

XRD crystalline component chemical composition. The chemical compositions of the XRD crystalline phases (Table 1) were calculated from phase abundances and phase compositions, with the latter determined by unit cell parameters (e.g., feldspar and olivine) and stoichiometry (e.g., hematite and magnetite) [2,3]. Because this method is not sensitive to minor substitutional impurities (e.g., Cr in pyroxene), The XRD calculated amorphous component is likely anomalously enriched in Cr_2O_3, TiO_2, and MnO. Note that the crystalline components are primary igneous minerals with minor secondary phases (e.g., anhydrite, bassanite, and akaganeite). The RN crystalline component is anhydrous within detection limits. JK and CB crystalline components are hydrous (e.g., bassanite and akaganeite).

The XRD crystalline component (exclusive of clay minerals) is 51 wt.%, 31 wt.%, and 31 wt.% of the bulk chemical composition for RN, JK, and CB, respectively (Table 1). The RN crystalline component is depleted in MgO and FeO relative to JK and CB because of the absence of olivine and enrichment of magnetite in the latter [2,3].

Smectite chemical composition. As discussed above, we used the chemical composition of a high-Fe saponite (griffithite) for the tri-octahedral smectite identified in JK and CB by CheMin (Table 1). The smectite abundance was constrained to 20 wt.% of bulk sample on the basis of the magnitude of the high-T H_2O release (smectite dehydroxylation) observed by SAM [4].

XRD amorphous component chemical composition. The chemical composition of the XRD amorphous component is calculated by mass-balance between the bulk and crystalline plus smectite compositions (Table 1). The proportion of amorphous component is significant and similar for RN, JK, and CB (~49 wt.%). The nature and number of amorphous phases that constitute the amorphous component is not unequivocally known. There can be contributions from crystalline components if present below CheMin detection limits.

The chemical compositions of the RN, JK, and CB amorphous components are broadly similar. All are Fe-rich, SiO_2 poor, and have $SiO_2/Al_2O_3 > 6$. The depletion of MgO in RN amorphous relative to JK and CB is evidence for the relative absence of olivine alteration in RN; griffithite itself can also be evidence for olivine in JK and CB progenitors [5]. These chemical trends indicate aqueous alteration under near neutral pH conditions. JK amorphous component is enriched in both CaO and SO_3 relative to RN and CB, suggesting amorphous Ca-sulfate is present.

The concentrations of perchlorate (Cl_2O_7) and sulfate (SO_3) inferred by SAM are consistent with amorphous phase chemistry because the total Cl and SO_3 concentrations (from APXS) are in excess of the SAM-determined concentrations (Table 1). The concentration of perchlorate inferred by SAM (~1 wt.% depending on the cation) is, if crystalline, at the CheMin detection limit [2]. The Cl excess for the CB amorphous component may suggest amorphous akaganeite in addition to the more crystalline form detected by CheMin, but this interpretation is equivocal.

Table 1. Chemical composition of bulk sample, XRD crystalline, smectite (Griffithite), and XRD amorphous components based on APXS, CheMin, and SAM datasets for Rocknest (RN), John Klein (JK), and Cumberland (CB).

	Bulk			XRD Crystalline			Griffithite	XRD Amorphous		
Element (wt.%)	RN	JK	CB	RN	JK	CB	JK & CB	RN	JK	CB
SiO_2	41.53	40.82	41.78	47.65	42.67	43.74	44.92	35.07	38.02	39.27
TiO_2	1.15	0.94	0.94	0.45	-0.02	0.57	0.00	1.89	1.92	1.56
Al_2O_3	9.13	8.41	8.32	12.26	12.48	12.38	8.60	5.83	5.80	5.65
Cr_2O_3	0.47	0.41	0.42	0.00	-0.01	-0.01	-0.01	0.98	0.83	0.86
$FeO+Fe_2O_3$	3.97	12.94	14.47	-0.04	-0.22	-0.23	14.91	8.21	20.32	23.54
Fe-CHMN	0.00	0.47	0.38	0.00	1.51	1.23	0.00	0.00	0.01	0.00
FeO-CHMN	6.90	3.24	3.63	13.46	10.53	11.74	0.00	-0.02	0.00	0.00
Fe_2O_3-CHMN	1.31	2.06	2.37	2.55	6.71	7.65	0.00	0.00	0.00	0.01
Fe_2O_3-npOx	6.40	0.58	0.86	-0.06	1.87	2.79	0.00	13.21	nd	nd
MnO	0.40	0.26	0.26	0.00	0.00	0.00	0.07	0.82	0.51	0.51
MgO	8.42	8.79	9.14	11.85	4.88	5.01	18.64	4.80	7.24	7.86
CaO	7.05	7.53	6.11	8.66	9.47	7.92	2.59	5.35	8.32	6.40
Na_2O	2.63	2.81	2.83	2.03	2.98	2.86	0.06	3.27	3.82	3.93
Na	0.00	0.04	0.03	0.00	0.13	0.08	0.00	0.00	0.00	0.00
K_2O	0.47	0.55	0.49	0.17	0.30	0.39	0.01	0.80	0.93	0.74
P_2O_5	0.91	0.90	0.92	-0.01	-0.02	-0.01	-0.01	1.88	1.84	1.90
SO_3	1.82	3.32	1.32	-0.02	1.08	0.73	-0.03	3.75	6.08	2.23
S-CHMN	0.00	0.33	0.28	0.00	1.07	0.74	0.00	0.00	0.00	0.10
SO_3-CHMN	0.46	0.95	0.28	0.89	3.10	0.91	0.00	0.00	-0.01	0.00
SO_3-SAM	3.00	0.35	0.20	-0.03	-0.01	0.00	0.00	6.19	0.72	0.41
Cl	0.44	0.50	0.98	0.00	0.33	0.31	-0.01	0.90	0.81	1.81
Cl_2O_7-SAM	0.40	0.12	0.95	0.00	0.00	-0.01	0.00	0.82	0.24	1.96
H_2O	2.00	2.06	1.89	-0.02	-0.04	-0.03	9.50	4.14	0.36	-0.01
H_2O-CHMN	0.00	0.12	0.14	0.00	0.40	0.49	0.00	0.00	0.00	-0.02
CO_2-SAM	0.90	0.70	0.25	-0.01	-0.01	0.00	-0.01	1.86	1.43	0.52
Sum	99.77	99.20	99.24	99.77	99.20	99.24	99.21	99.77	99.19	99.23
$\sum(Fe+FeO+Fe_2O_3)$	18.58	19.27	21.71	15.91	20.40	23.18	14.91	21.40	20.32	23.55
$\sum(SO_3)$	5.28	4.95	2.08	0.85	5.25	2.39	-0.04	9.95	6.79	2.74
Whole Sample	100.0	100.0	100.0	51.3	30.7	30.9	20.0	48.7	49.3	49.1

Notes: APXS data from [1,3,5], CheMin data from [2] and [3], and SAM data from [4]. For JK and CB, the smectite is interpreted as Griffithite (see text) with chemistry from [5]. Griffithite abundance (20 wt.%) is from [4].

References: [1] Blake *et al.* (2013) *Science, 341*, DOI:10.1126/science.1239505. [2] Bish *et al.* (2013) *341*, DOI:10.1126/science.1238932. [3] Vaniman *et al.* (2013) *Science*, DOI:10.1126/science.1243480. [4] Ming *et al.* (2013) *Science*, DOI:10.1126/science.1238937. [5] Treiman *et al.* (2014) *Am. Mineral.*, submitted.