

ELECTONIC ANNEX TO

**Smectite formation in the presence of sulfuric acid: Implications for acidic
smectite formation on early Mars**

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Figure section contains four figures. Figure EA-1 shows polished section of smectite/glass aggregate. Figure EA-2 shows calculated crust production on Mars; Figure EA-3 shows XRD data for clay fractions separated from pH_{14d} 3.1 and 8.4 samples and Figure EA-4 is dissolved Al and Fe data.

Table section contains three tables. Table EA-1 shows composition of Adirondack rock from Gusev crater as well as synthetic Adirondack basalt simulant. Table EA-2 shows fitted Mössbauer parameters. Table EA-3 has results of microprobe analysis of glass phase in unaltered Adirondack basalt simulant, composition of formed smectite and calculated smectite structural formula.

Text EA-1 contains detailed analysis of Fe(II) oxidative hydrolysis model previously proposed as a source of acidity on early Mars.

Text EA-2 explains calculations of the amount of H⁺ required for complete neutralization of Na, Ca and Mg in basalt of Adirondack composition.

Text EA-3 explains calculations of the amount of H⁺ required to neutralize all Na, Ca and Mg in basalt of varying thickness.

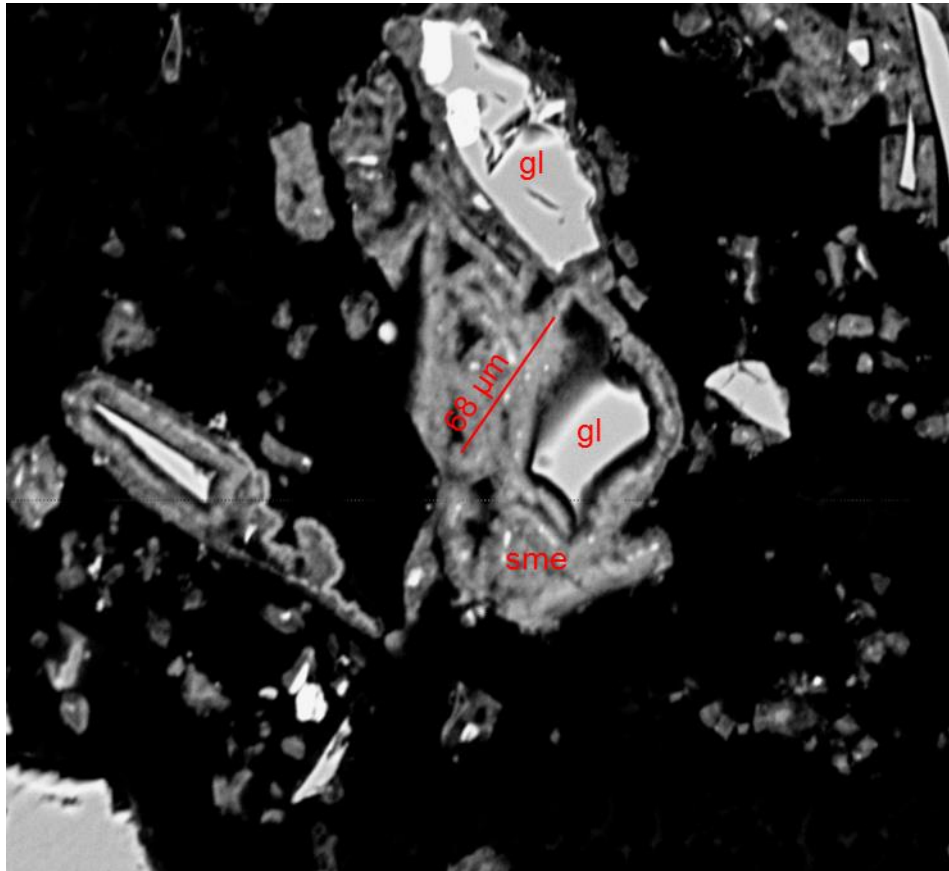


Figure EA-1. An example of a polished section of smectite (sme)/glass (gl) aggregate observed at $\text{pH}_{14\text{d}}$ 8.4. Chemical composition of smectite was measured along the line in the inner part of smectite.

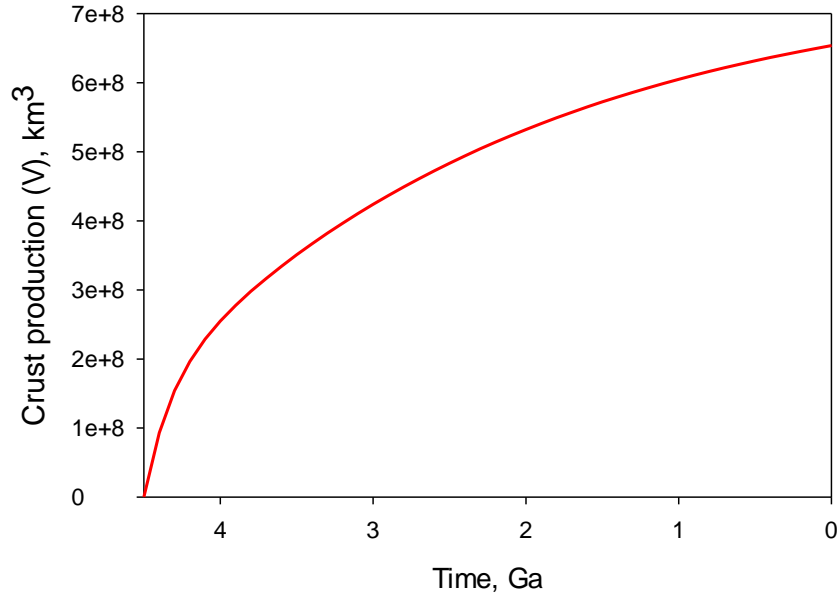


Figure EA-2. Crust production on Mars from 4.5 Ga to present (Hirschmann and Withers, 2008).

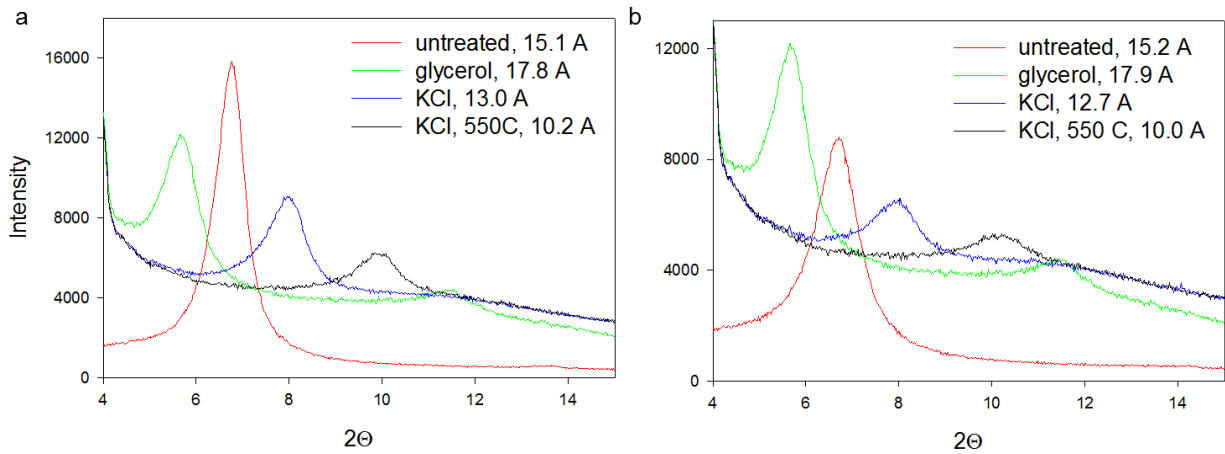


Figure EA-3. Position of 001 peak in clay size fraction of (a) pH_{14d} 8.4 and (b) pH_{14d} 3.1 samples. Expansion of the 001 XRD peaks to ~18 Å after glycerol treatment of the clay size fraction and 001 peak collapse to ~13 Å at room temperature upon KCl addition and further collapse to ~10 Å after heating at 550 °C confirmed the formation of smectite.

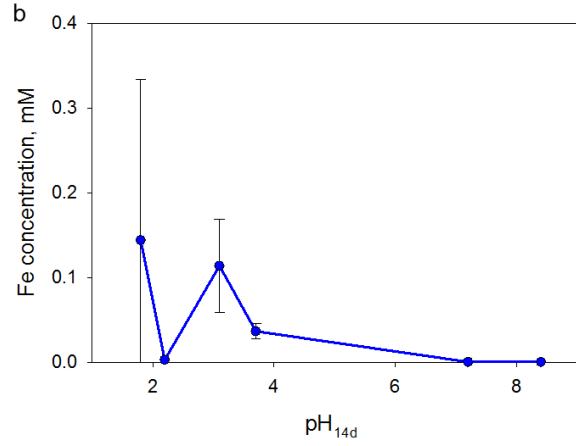
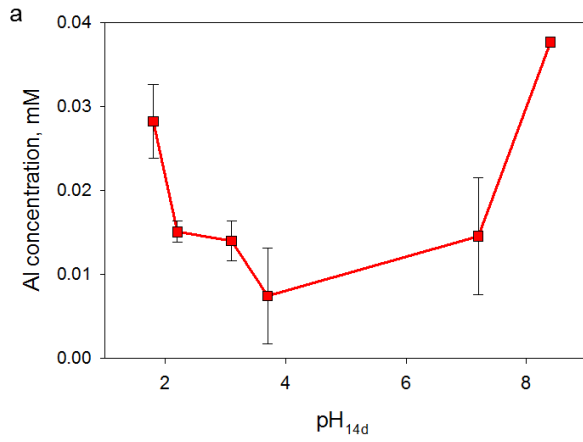


Figure EA-4. Dissolved concentrations of (a) Al and (b) Fe in Adirondack basalt simulant suspensions as a function of pH_{14d}.

Table EA-1. Compositions (wt%) of Adirondack basaltic rock in Gusev crater (McSween et al., 2006) and phases detected in the Adirondack basalt simulant (Peretyazhko et al., 2016).

	Adirondack at Gusev	Adirondack basalt simulant Glass phase	Adirondack basalt simulant Olivine phase	Adirondack basalt simulant Chromite phase
SiO ₂	45.30	47.27 ± 0.65	36.56 ± 0.20	0.24 ± 0.15
TiO ₂	0.49	0.57 ± 0.12	0.03 ± 0.02	0.94 ± 0.45
Al ₂ O ₃	10.42	11.67 ± 0.65	0.11 ± 0.04	14.89 ± 2.15
FeO	19.34	18.16 ± 0.59	27.67 ± 0.99	36.91 ± 4.32
Cr ₂ O ₃	0.62	0.11 ± 0.03	0.16 ± 0.08	33.97 ± 4.54
MnO	0.42	0.42 ± 0.03	0.61 ± 0.00	0.38 ± 0.03
MgO	11.90	8.42 ± 0.96	33.21 ± 0.84	7.99 ± 0.94
CaO	7.76	8.86 ± 0.42	0.48 ± 0.06	0.24 ± 0.07
Na ₂ O	2.09	2.57 ± 0.17	0.020 ± 0.0017	0.01 ± 0.01
K ₂ O	0.03	0.076 ± 0.012	0.0032 ± 0.0045	0.0056 ± 0.0059
NiO	0.32	0.09 ± 0.04	0.72 ± 0.12	0.50 ± 0.08
P ₂ O ₅	0.54	0.38 ± 0.04	0.09 ± 0.11	0.38 ± 0.04
Total	99.81	98.61 ± 0.42	96.25 ± 14.16	96.73 ± 12.68

Table EA-2. Mössbauer parameters of unaltered and 14d-incubated Adirondack basalt simulant.

Sample and Subspectra	Cation	CS ¹ mm/s	QS ¹ mm/s	FWHM ¹ mm/s	B _{hf} ¹ T	A ¹ %	Fe(III) /ΣFe	Assignment
Unaltered²							0.12	
Doublet 3D1	Fe(III)	0.34	1.15	0.69		12		Glass
Doublet 2D1	Fe(II)	1.01	1.58	0.57		36		Glass
Doublet 2D2	Fe(II)	1.08	2.16	0.47		33		Glass
Doublet 2D3	Fe(II)	1.14	2.89	0.33		19		Olivine
pH_{14d} 8.4							0.48	
Doublet 2D1	Fe(II)	0.93	1.75	0.55		14		Glass
Doublet 2D2	Fe(II)	1.03	2.20	0.40		13		Glass
Doublet 2D3	Fe(II)	1.14	2.97	[0.29] ³		15		Olivine
Doublet 3D2	Fe(III)	0.41	0.70	0.67		46		Smectite
Doublet 2D4	Fe(II)	1.09	2.66	[0.29]		10		Smectite
Sextet 3S1	Fe(III)	[0.37] ⁴	[-0.22]		48.4	2		Hematite
pH_{14d} 3.7							0.38	
Doublet 2D1	Fe(II)	0.91	1.67	0.60		19		Glass
Doublet 2D2	Fe(II)	1.02	2.07	0.44		19		Glass
Doublet 2D3	Fe(II)	1.13	2.93	0.31		13		Olivine
Doublet 3D2	Fe(III)	0.45	0.63	0.76		30		Smectite
Doublet 2D4	Fe(II)	1.07	2.55	0.33		11		Smectite
Sextet 3S1	Fe(III)	[0.37]	[-0.22]		49.4	8		Hematite
pH_{14d} 3.1							0.35	
Doublet 2D1	Fe(II)	0.89	1.56	0.60		19		Glass
Doublet 2D2	Fe(II)	1.01	1.94	0.43		23		Glass
Doublet 2D3	Fe(II)	1.11	2.90	0.31		8		Olivine
Doublet 3D2	Fe(III)	0.48	0.54	0.76		23		Smectite
Doublet 2D4	Fe(II)	1.04	2.42	0.38		15		Smectite
Sextet 3S1	Fe(III)	[0.37]	[-0.22]		48.4	12		Hematite
pH_{14d} 1.8							0.44	
Doublet 2D1	Fe(II)	0.95	1.67	0.57		25		Glass
Doublet 2D2	Fe(II)	1.02	2.11	0.41		21		Glass
Doublet 3D2	Fe(III)	0.46	0.62	0.76		29		Altered glass ⁵
Doublet 2D4	Fe(II)	1.03	2.60	0.36		10		Altered glass
Sextet 3S1	Fe(III)	[0.37]	[-0.22]		47.7	15		Hematite

¹ CS = center shift with respect to metallic Fe foil; QS = quadrupole splitting; A = subspectral area, f-factor corrected; FWHM = full width at half maximum; B_{hf} -magnetic hyperfine field strength. ² From Peretyazhko et al (2016). ³ Values in square brackets were held constant during the fit. ⁴ For the hematite sextet, CS and QS were fixed to literature values (Morris et al., 1985); peak areas were constrained to 3:x:1:1:x:3 with x variable; FWHM decreased symmetrically toward zero velocity; and a skewed Lorentzian lineshape was used. ⁵ 3D2 and 2D4 doublets are consistent with values reported for smectite. However, smectite was not detected by XRD in this sample and the doublets were assigned to altered glass. Uncertainty: CS = ±0.02 mm/s; QS = ±0.02 mm/s; FWHM = ±0.02 mm/s B_{hf} = ±0.2 T; A = ±2 %; Fe(III)/ΣFe = ±0.02.

Table EA-3. Compositions of glass phase of unaltered Adirondack basalt simulant and smectite (in wt%) and calculated smectite structural formula based on $O_{20}(OH)_4$ stoichiometry. High uncertainties of the measured data and low values of total elemental content (due to high water content in smectite) did not allow accurate calculations of smectite compositions.

	Glass phase	pH _{14d} 8.4	pH _{14d} 7.2 ¹	pH _{14d} 3.7	pH _{14d} 3.1
Na	1.91 ± 0.13	0.50 ± 0.23	0.11 ± 0.06	0.25 ± 0.05	0.82 ± 0.29
K	0.06 ± 0.01	0.25 ± 0.07	0.17 ± 0.09	0.05 ± 0.01	0.07 ± 0.02
Ca	6.33 ± 0.30	1.24 ± 0.33	1.11 ± 0.42	0.92 ± 0.23	4.26 ± 1.20
Mg	5.08 ± 0.58	5.97 ± 0.71	5.12 ± 0.80	7.33 ± 1.41	3.71 ± 0.12
Fe	14.11 ± 0.46	11.91 ± 0.75	14.22 ± 2.72	9.86 ± 0.64	8.18 ± 2.65
Al	6.18 ± 0.17	5.66 ± 0.96	5.58 ± 1.17	6.31 ± 0.46	4.60 ± 0.85
Si	22.10 ± 0.30	20.19 ± 1.28	19.02 ± 1.41	19.73 ± 1.23	18.84 ± 1.85
Mn	0.33 ± 0.02	0.30 ± 0.04	0.30 ± 0.04	0.20 ± 0.03	0.26 ± 0.07
Ni	0.07 ± 0.03	0.09 ± 0.06	0.09 ± 0.06	0.32 ± 0.10	0.09 ± 0.06
Ti	0.34 ± 0.07	0.21 ± 0.08	0.26 ± 0.17	0.25 ± 0.05	0.33 ± 0.05
Cr	0.07 ± 0.02	0.08 ± 0.07	0.15 ± 0.23	0.05 ± 0.01	0.10 ± 0.04
O	41.85 ± 0.29	36.53 ± 1.69	35.22 ± 0.86	36.67 ± 1.27	33.09 ± 0.97
TOTAL	98.44 ± 0.42	82.87 ± 3.54	81.36 ± 1.23	81.94 ± 2.37	74.33 ± 1.83
<i>Tetrahedral</i>					
Si		7.04 ± 0.45	6.91 ± 0.51	6.84 ± 0.43	7.62 ± 0.75
Al		0.96 ± 0.45	1.09 ± 0.51	1.16 ± 0.43	0.38 ± 0.75
Charge		-0.95 ± 0.63	-1.09 ± 0.72	-1.16 ± 0.60	-0.37 ± 1.06
<i>Octahedral</i>					
Al		1.10 ± 0.56	1.02 ± 0.68	1.11 ± 0.46	1.56 ± 0.83
Mg		2.42 ± 0.29	2.16 ± 0.34	2.95 ± 0.57	1.74 ± 0.05
Fe			2.59 ± 0.50		
Fe(II)		0.36 ± 0.13		0.45 ± 0.11	0.65 ± 0.54
Fe(III)		1.72 ± 0.13		1.26 ± 0.11	1.01 ± 0.54
Ti		0.04 ± 0.02	0.05 ± 0.04	0.05 ± 0.01	0.08 ± 0.01
Mn		0.05 ± 0.01	0.06 ± 0.01	0.03 ± 0.00	0.05 ± 0.01
Ni		0.02 ± 0.01	0.02 ± 0.01	0.05 ± 0.02	0.02 ± 0.01
Cr		0.01 ± 0.01	0.01 ± 0.05	0.004 ± 0.002	0.01 ± 0.01

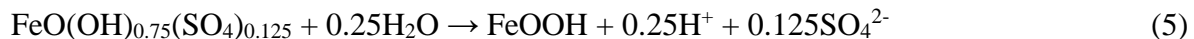
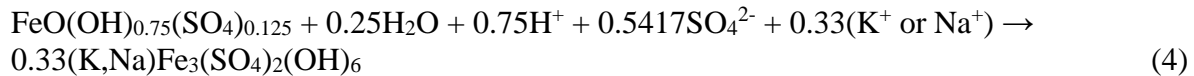
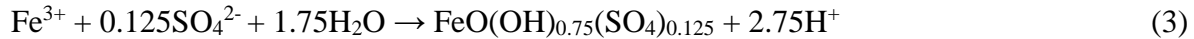
Σ Cations	5.72 ± 0.65	5.91 ± 0.91	5.91 ± 0.74	5.11 ± 0.99
Charge	2.36 ± 0.66		2.30 ± 0.75	0.97 ± 1.13
<hr/> <i>Interlayer</i> <hr/>				
K	0.06 ± 0.02	0.04 ± 0.02	0.01 ± 0.01	0.02 ± 0.01
Na	0.21 ± 0.10	0.05 ± 0.03	0.10 ± 0.02	0.40 ± 0.14
Ca	0.03 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Charge	0.34 ± 0.10	0.14 ± 0.04	0.13 ± 0.02	0.45 ± 0.14
Total charge	1.74 ± 0.92		1.27 ± 0.96	1.03 ± 1.56

¹ Sample pH_{14d} 7.2 was not analyzed by Mössbauer spectroscopy. Octahedral and total charge were not calculated for this sample because Fe(II) and Fe(III) were not measured.

Text EA-1: Fe(II) oxidative hydrolysis as a source of acidity on early Mars

Acidity generation through Fe(II) oxidative hydrolysis has been proposed as a source of acidity on early Mars (Hurowitz et al., 2010). According to the model, circum-neutral Fe(II)-containing solution was generated during dissolution of basalt under anoxic conditions. Upwelling of Fe(II)-rich groundwater to oxic environments on the surface leads to oxidation of Fe(II) to Fe(III) followed by Fe(III) hydrolysis, release of H⁺ and precipitation of Fe(III) secondary minerals detected at Meridiani Planum by Mössbauer spectroscopy [nanophase iron(III) (hydr)oxides interpreted as shwertmannite, jarosite ((K,Na)Fe₃(SO₄)₂(OH)₆) and hematite (α-Fe₂O₃)] (Morris et al., 2006).

The reactions below summarize the reactions describing Fe(II) oxidative hydrolysis model. The reactions closely follow the sequence developed by Hurowitz et al., (2010) with the important exception that the dissolution of basalt is included (eq. 1). Aqueous Fe(II) can be released into groundwater during dissolution of olivine and pyroxene which are the predominant Fe(II)-silicates in basalts on Mars (Burns, 1993). For simplicity the Fe(II) dissolution (eq. 1) is written for olivine Fe(II)-end member fayalite (Fe₂SiO₄). The dissolved Fe(II) is then oxidized to Fe(III) and formation of schwertmanite, hematite and jarosite occurs (i.e., eqs. 2-6 are from Hurowitz et al., (2010)):



Without including the dissolution reaction (eq.1), Hurowitz et al., (2010) calculated that 2.63-3.36 mol_{H⁺}/kg_{outcrop} could be produced during Fe(II) oxidation and Fe(III) hydrolysis (eqs. 2-6). The produced H⁺ remained in excess after reacting with all base anions detected in the outcrop (SO₄²⁻, Cl⁻, PO₄³⁻, CO₃²⁻) at pH 2 (0.5-1.61 mol_{H⁺}/kg_{outcrop}) and pH 4 (1.82-2.59 mol_{H⁺}/kg_{outcrop}) (Hurowitz et al., 2010).

We have recalculated the H⁺ production reactions including the full reaction sequence from dissolution to precipitation (i.e., eqs. 1-6) following the description of acidity calculations found in Hurowitz et al., (2010). Briefly, Fe abundance (in mol/kg) in schwertmannite, jarosite and hematite was first calculated using total Fe content determined by alpha-particle X-ray spectrometer (APXS) and Mössbauer subspectral areas (Table EA-4). Then, the cumulative H⁺

reaction coefficient was calculated for formation of 1 mole jarosite, hematite or schwertmannite using reactions (1)-(6). For instance, for formation of 1 mole schwertmannite, 2 moles of H⁺ is consumed in fayalite dissolution (1), then 1 mole of H⁺ is consumed during Fe oxidation (2) and 2.75 moles of H⁺ is produced during schwertmannite precipitation (3) resulting in cumulative H⁺ reaction coefficient of -0.25 (-2-1+2.75). The negative value indicates proton consumption and generation of alkalinity. Similarly, for hematite formation, the sum of reactions (1), (2), (3) and (5) has a cumulative H⁺ reaction coefficient of 0 (reaction of goethite transformation into hematite (6) was not included because no protons are consumed or produced), and for jarosite the sum of reactions (1), (2), (3), (4) has a cumulative H⁺ reaction coefficient of -1. Finally, the obtained cumulative H⁺ reaction coefficient (-0.25 for schwertmannite, 0 for hematite and -1 for jarosite) was multiplied by the calculated number of Fe moles associated with hematite, jarosite and schwertmanite at Meridiani Planum (Table EA-4) to obtain H⁺ concentration (Table EA-5).

Summarizing, we calculate that the sequence of Fe(II) dissolution, oxidation to Fe(III), and Fe(III) hydrolysis will result in consumption, rather than production, of H⁺ (i.e., negative total H⁺ concentration, Table EA-5).

Table EA-4. Summary of total Fe determined by AXPS, Mössbauer subspectral areas and calculated Fe content in jarosite (Jar), hematite (Hem) and schwertmannite (Sch) at Meridiani Planum [data from (Hurowitz et al., 2010)].

Sample name, sol# ¹	APXS Total Fe, mol/kg	Mössbauer subspectral area			Fe in Fe(III) phases, mol/kg		
		Sch	Jar	Hem	Sch	Jar	Hem
McKittrick_RAT, 31	2.30	22	26	39	0.51	0.60	0.90
Guadalupe_RAT, 36	2.06	16	38	36	0.33	0.78	0.74
Mojo2_RAT, 45	2.13	25	22	38	0.53	0.47	0.81
Golf_Post_RAT_FRAM, 87	2.19	20	33	37	0.44	0.72	0.81
LionStone_Numa_RAT, 108	1.99	22	30	34	0.44	0.60	0.68
Kentucky_Cobble_Hill2_RAT, 145	2.05	20	28	35	0.41	0.57	0.72
Virginia_RAT, 147	2.16	19	28	35	0.41	0.60	0.76
Ontario_London_RAT, 149	2.02	19	27	35	0.38	0.55	0.71
Grindstone_RAT, 153	2.06	20	28	34	0.41	0.58	0.70
Kettlestone_RAT, 155	2.12	21	29	32	0.45	0.61	0.68
Millstone_Dramensfjord_RAT, 162	2.20	18	27	33	0.40	0.59	0.73
Diamond_Jenness_Holman3_RAT	2.15	18	29	41	0.39	0.62	0.88
MacKenzie_Campell_RAT, 184	2.17	19	31	34	0.41	0.67	0.74
Inuvik_Toruyuktuk_RAT, 187	2.38	18	26	40	0.43	0.62	0.95
Bylot_RAT, 195	2.46	14	30	41	0.34	0.74	1.01
Escher_Kirchner_RAT, 220	2.19	20	30	35	0.44	0.66	0.77
Wharenhui_RAT, 312	2.10	19	28	34	0.40	0.59	0.71
Gagarin_RAT, 403	2.21	24	32	37	0.53	0.71	0.82
IceCream_RAT, 548	2.20	19	32	36	0.42	0.70	0.79

¹ Sample name and sol number for the Mars Exploration Rover *Opportunity*.

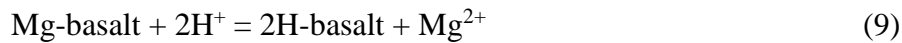
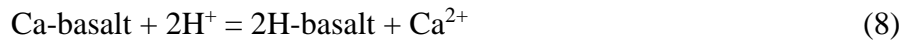
Table EA-5. Total H⁺ concentration produced by reactions 1-6 at Meridiani Planum (negative concentration indicates proton consumption and positive concentration indicates proton production).

Sample name, sol#	H ⁺ , mol/kg			Total H ⁺ mol/kg
	Sch 1+2+3 ¹	Jar 1+2+3+4 ¹	Hem 1+2+3+5 ¹	
McKittrick_RAT, 31	-0.13	-0.60	0	-0.73
Guadalupe_RAT, 36	-0.08	-0.78	0	-0.86
Mojo2_RAT, 45	-0.13	-0.47	0	-0.60
Golf_Post_RAT_FRAM, 87	-0.11	-0.72	0	-0.83
LionStone_Numa_RAT, 108	-0.11	-0.60	0	-0.71
Kentucky_Cobble_Hill2_RAT, 145	-0.10	-0.57	0	-0.67
Virginia_RAT, 147	-0.10	-0.60	0	-0.70
Ontario_London_RAT, 149	-0.10	-0.55	0	-0.65
Grindstone_RAT, 153	-0.10	-0.58	0	-0.68
Kettlestone_RAT, 155	-0.11	-0.61	0	-0.72
Millstone_Dramensfjord_RAT, 162	-0.10	-0.59	0	-0.69
Diamond_Jenness_Holman3_RAT	-0.10	-0.62	0	-0.72
MacKenzie_Campell_RAT, 184	-0.10	-0.67	0	-0.77
Inuvik_Toruyuktuk_RAT, 187	-0.11	-0.62	0	-0.73
Bylot_RAT, 195	-0.09	-0.74	0	-0.83
Escher_Kirchner_RAT, 220	-0.11	-0.66	0	-0.77
Wharenhui_RAT, 312	-0.10	-0.59	0	-0.69
Gagarin_RAT, 403	-0.13	-0.71	0	-0.84
IceCream_RAT, 548	-0.10	-0.70	0	-0.81

¹ Reactions used to calculate total H⁺.

Text EA-2: H⁺ required for complete neutralization of Na, Ca and Mg in basalt of Adirondack composition.

Protons are neutralized by Ca, Mg and Na via proton exchange reactions leading first to formation of an altered hydrated silica layer enriched in Fe and Al by schematic reactions:



Steps for calculating H⁺ required for complete neutralization of Na, Ca and Mg in basalt of Adirondack composition are summarized in the Table EA-6. If the amount of H⁺ added to basalt exceeds the amounts of Na, Ca and Mg than aqueous solution remains acidic. Alkaline conditions can be achieved if the amount of added H⁺ is lower than the cation content.

Table EA-6. Calculations of amount of H⁺ for complete neutralization of Na, Ca and Mg in Adirondack.

Oxide	wt% ¹	g/kg	mol _{oxide} /kg	Element	mol _{element} /kg	Reacted H ⁺ , mol _{H⁺} /kg ²
MgO	11.90	119	2.975	Mg	2.975	5.950
CaO	7.76	77.6	1.386	Ca	1.386	2.771
Na ₂ O	2.09	20.9	0.337	Na	0.674	0.674
						ΣH⁺ = 9.395
						mol_{H⁺}/kg ≈ 9.4
						mol_{H⁺}/kg

¹Data from McSween et al.,(2006) ; ²calculated using eqs.7-9.

Text EA-3: H⁺ to neutralize Na, Ca and Mg in basalt of varying thickness.

We estimated basalt thickness over entire planet required to neutralize 1.6×10^{20} moles of H⁺ produced on early Mars through reaction with Na, Ca and Mg in basalt (eqs. 7-9). First, basalt volume was calculated by the following equation:

$$Vol = \frac{4}{3}\pi(R^3 - (R - h)^3) \quad (10)$$

where R is Mars radius of 3390000 m and h is a thickness of altered layer of basalt. Then we calculated the weight of basalt of varying thickness:

$$m = \rho * Vol \quad (11)$$

where ρ is an average basalt density of 2800 kg/m³.

Finally the total amount of H⁺ needed for complete neutralization of Na, Ca and Mg was obtained using the calculated basalt weight and the amount of H⁺ for neutralization of 1 kg basalt (9.40 mol_{H⁺}/kg) by the following equation:

$$\text{Total H}^+ = 9.40 \text{ mol}_{\text{H}^+}/\text{kg} * m \quad (12)$$

The calculated results summarized in Table EA-7 revealed that 1.6×10^{20} moles H⁺ would be sufficient for complete neutralization of Ca, Mg and Na and phyllosilicate formation in 42 m thick basalt layer over entire planet.

Table EA-7. Calculated amounts of H⁺ required for complete neutralization of Na, Ca and Mg in basalt of Adirondack composition.

Basalt thickness (h), m	Basalt weight (m), kg	Total H ⁺ , moles
10	$4.0 \cdot 10^{18}$	$3.8 \cdot 10^{19}$
30	$1.2 \cdot 10^{19}$	$1.1 \cdot 10^{20}$
42	$1.7 \cdot 10^{19}$	$1.6 \cdot 10^{20}$
50	$2.0 \cdot 10^{19}$	$1.9 \cdot 10^{20}$
100	$4.0 \cdot 10^{19}$	$3.8 \cdot 10^{20}$

References

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