

Manganese Mobility in Gale Crater, Mars: Leached Bedrock and Localized Enrichments

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Additional Supporting Information (File uploaded separately)

Data Set S1

Introduction

The supporting information includes one separately uploaded Comma-Separated Value file (CSV) containing Data Sets S1. An explanation for the columns in Data Set S1 is presented in this document. The data were acquired with the methods described in the manuscript text.

Explanation for Data Set S1

Data Set S1: APXS results for sols 0-3076 of the MSL mission. The data are available separately in the supporting information file named "Berger_Mn_DS01_sol3076-v5.csv".

Explanation of columns in Data Set S1

Column name	Explanation
Sol	Martian solar days since <i>Curiosity</i> landed on August 6, 2012. One sol = 24.7 hours.
Target	The name of the APXS target. Names are taken from geographical place names according to naming conventions (e.g., Vasavada et al., 2014) and do not necessarily have any significance to the target itself. APXS target names are applied to a location on the martian surface with a footprint approximately less than 5 cm in diameter, with few exceptions. When other instruments analyze the same location, the same target name is used, with some exceptions. The APXS target names are appended with modifying information (e.g., <i>_raster1</i> , <i>_raster2</i>) when applicable, and the appended text may or may not correspond with appended text used by other instruments for the same target. Names are the same in the APXS data set in the Planetary Data System (DOI 10.17189/1518757).
Strat_group	Stratigraphic group name.
Strat_fm	Stratigraphic formation name.
Strat_mbr	Stratigraphic member name. See Figure 1.
Informal_waypoint/ outcrop_name	Informal name periodically assigned to waypoints and outcrop but is not necessarily associated with an APXS target name.
Ca-S_notes	Indicates when prominent white Ca-sulfate veins (SO ₃ > 15wt%) are confirmed to be in the APXS field of view, and notes if they are crosscutting or concordant with the bedding planes.
Preparation_method	Describes the preparation method with the abbreviations explained in Table S6.
Quality	Indicates targets with low quality due to sub-standard statistics or spectral resolution (FWHM Fe K _α >210 eV).
Duplicate_measurement	Indicates duplicate measurement of one target as described in the text.
Fit_Type	Name of the fit method as described for the MSL APXS in the Planetary Data System (DOI 10.17189/1518757). It specifies the fit routine type and version used for the calculation of concentrations released herein.
Start_Time	Sol number and local mean solar time (24-hour clock format) at the beginning of the APXS integration. For example, 00046M11:43:31 denotes a start time on sol 46 at 11 hours, 43 minutes, and 31 seconds Mars time in Gale crater.
Latitude	Latitude of the APXS target in degrees ^a .
Longitude	Longitude of the APXS target in degrees ^a .
Elevation	Elevation of the APXS target in meters ^a .
Northing	Northing coordinate of the target location in units of meters ¹ . For drilled samples that were transported inside the sampling subsystem some distance away from the drill site location, then dumped on the ground for an APXS measurement: the coordinate shown in this column is where the sample was collected, NOT where it was dumped.
Easting	Easting coordinate of the target location in units of meters ¹ . For drilled samples that were transported inside the sampling subsystem some distance away from the drill site location, then dumped on the ground for an APXS measurement: the coordinate shown in this column is where the sample was collected, NOT where it was dumped.

Elevation_2	Elevation in meters ¹ . For drilled samples that were transported inside the sampling subsystem some distance away from the drill site location, then dumped on the ground for an APXS measurement: the elevation shown in this column is where the sample was collected, NOT where it was dumped.
Standoff_distance	Estimated distance of the APXS sensor head from the mean surface of the target, in centimeters.
SH_Temp	Average temperature of the sensor head chassis during the integration in degrees C.
Lifetime	Duration of the APXS integration after removing poorer quality data. APXS integrations are time-partitioned into multiple blocks to allow for the selective removal of data of a poorer quality. Factors that can affect whether a block is accepted or rejected include its resolution (i.e. temperature), instrument lock-up, detector high voltage stabilization, etc.
FWHM	Full width at half-maximum at the Fe K-alpha peak, in eV.
Na2O	Oxide concentration in weight percent.
Na2O_err	Statistical fitting error (two sigma) in weight percent.
MgO	Oxide concentration in weight percent.
MgO_err	Statistical fitting error (two sigma) in weight percent.
Al2O3	Oxide concentration in weight percent.
Al2O3_err	Statistical fitting error (two sigma) in weight percent.
SiO2	Oxide concentration in weight percent.
SiO2_err	Statistical fitting error (two sigma) in weight percent.
P2O5	Oxide concentration in weight percent.
P2O5_err	Statistical fitting error (two sigma) in weight percent.
SO3	Oxide concentration in weight percent.
SO3_err	Statistical fitting error (two sigma) in weight percent.
Cl	Element concentration in weight percent.
Cl_Err	Statistical fitting error (two sigma) in weight percent.
K2O	Oxide concentration in weight percent.
K2O_err	Statistical fitting error (two sigma) in weight percent.
CaO	Oxide concentration in weight percent.
CaO_err	Statistical fitting error (two sigma) in weight percent.
TiO2	Oxide concentration in weight percent.
TiO2_err	Statistical fitting error (two sigma) in weight percent.
Cr2O3	Oxide concentration in weight percent.
Cr2O3_err	Statistical fitting error (two sigma) in weight percent.
MnO	Oxide concentration in weight percent.
MnO_err	Statistical fitting error (two sigma) in weight percent.
FeO	Oxide concentration in weight percent.
FeO_err	Statistical fitting error (two sigma) in weight percent.
Ni	Element concentration in parts per million.
Ni_err	Statistical fitting error (two sigma) in parts per million.
Zn	Element concentration in parts per million.
Zn_err	Statistical fitting error (two sigma) in parts per million.
Br	Element concentration in parts per million.
Br_err	Statistical fitting error (two sigma) in parts per million.

¹<https://an.rsl.wustl.edu/mer/help/Content/Using%20the%20Notebook/Main%20sections/Maps/Traverse%20map.htm> "The base map is a subset of the Gale_C_PSP_010573_1755_010639_1755_25cm image georeferenced by Tim Parker and Fred Calef for their localization activities. The traverse is generated by applying the best_tactical places solution updates to the raw rover telemetry."

Table S1: APXS precision error and accuracy for a typical rock target

	Concentration: Stoer ^a drill fines (wt%)	Statistical fitting error (wt%)	Accuracy ^b (%)	Nominal limit of detection ^b (wt%)
SiO ₂	44.1	0.54	3	1
TiO ₂	1.03	0.03	20	0.2
Al ₂ O ₃	8.75	0.19	7	1
FeO	21.5	0.26	7	0.03
MnO	0.17	0.01	8	0.05
MgO	4.72	0.17	14	1
CaO	6.44	0.07	7	0.2
Na ₂ O	2.45	0.14	11	1
K ₂ O	0.91	0.04	15	0.2
P ₂ O ₅	0.84	0.05	15	0.3
Cr ₂ O ₃	0.34	0.01	19	0.05
Ni (ppm)	915	50	16	50
Zn(ppm)	850	30	16	30
SO ₃	7.59	0.10	15	0.2
Cl	0.89	0.02	30	0.2
Br (ppm)	45	5	20	20

^aStoer_dump_centre is one measurement on sol 2154 that is representative of the statistical error for an overnight measurement. This is a high quality 7.5 h measurement with a standoff distance of ~8 mm and a FWHM (Fe K α) of 149 eV.

^bAccuracy and limit of detection determined by APXS calibration (Gellert et al., 2006; Gellert & Clark, 2015; VanBommel et al., 2019).

Table S2: Table of image metadata for Figure 3

Fig. 3 panel	Sol ^a	Target name	Camera	Data product/sequence number	Image adjustments ^b	MAHLI focus motor count	MAHLI standoff (cm)	MAHLI resolution ^c (μm/pixel)	Image credit
a	609	Stephen	Mastcam	Sequence mcam02569	Stretch RGB				MSSS
b	627	Stephen	MAHLI	0627MH0001900010203555C00	Stretch RGB	13009	25	102	MSSS
c	1685	Newport Ledge	Navcam	N_R000_1685_ILT062CYP_S_3188_UNCORM2_2PCT	Stretch 2%				JPL-Caltech
c	1686	Newport Ledge	Mastcam	Sequence mcam08769	Stretch RGB				MSSS
d	1686	Newport Ledge	MAHLI	1686MH0001900010603710C00		13018	25	100	MSSS
e	1726	Jones Marsh	Navcam	N_L000_1726_ILT064CYL_S_000_UNCORM1	Stretch 2%				JPL-Caltech
f	1727	Jones Marsh	MAHLI	1727MH0001530000404803R00 1727MH0001530000404805R00 1727MH0001530000404807R00	Stretch RGB	13862	5	35	MSSS
g	2664	Dunbartonshire refined	Mastcam	Sequence mcam13965	Stretch RGB				MSSS
h	2690	Dunbartonshire refined	MAHLI	2690MH0001900011001873C00	Stretch RGB	13017	25	100	MSSS
i	2857	Ayton	MAHLI	2857MH0007060011003305C00	Stretch RGB	13019	25	100	MSSS

^aThis is the sol that the image was taken. Typically, the image sol is before or on the APXS sol; some images were after APXS.

^bStretch RGB means that the brightness histograms of each RGB channel was adjusted to fill the full range of values from 0 to 255.

^cThe MAHLI resolution applies to the raw data product. Images in Figure 3 have lower resolutions to reduce file size.

Table S3: Summary of 21 measurements of 12 targets with MnO > 1 wt%

sol	target	Description ^a	Fig. 3 panel ^b	Other enrichments	MnO (wt%)	P2O5 (wt%)	Cl (wt%)	FeO (wt%)	Zn (ppm)
2691	Dunbartonshire_ref ined	Vein	h	Fe, Cl	6.33 ± 0.13	0.62 ± 0.05	1.97 ± 0.04	39.65 ± 0.46	1593 ± 50
2642	Abernethy	Vein		Fe, Cl, Zn	5.11 ± 0.11	0.69 ± 0.05	1.81 ± 0.05	40.12 ± 0.46	2630 ± 80
629	Stephen_Raster3	Vein or coating	b	Zn, Cl	4.87 ± 0.09	0.69 ± 0.07	3.19 ± 0.09	20.64 ± 0.26	8490 ± 255
627	Stephen	Vein or coating	b	Zn, Cl	4.05 ± 0.03	0.7 ± 0.05	3.36 ± 0.04	21.58 ± 0.26	8156 ± 245
1727	Jones_Marsh	Crust or coating	e, f	P, Cl	3.99 ± 0.09	7.56 ± 0.4	3.1 ± 0.09	19.84 ± 0.26	1265 ± 50
629	Stephen_Raster1	Vein or coating	b	Zn, Cl	3.88 ± 0.07	0.76 ± 0.07	3.26 ± 0.08	21.21 ± 0.26	7160 ± 215
629	Stephen_Raster4	Vein or coating	b	Zn, Cl	3.41 ± 0.08	0.74 ± 0.07	3.12 ± 0.07	20.96 ± 0.26	6777 ± 205
629	Stephen_Raster2	Vein or coating	b	Zn, Cl	3.34 ± 0.05	0.65 ± 0.07	3.44 ± 0.09	21.48 ± 0.26	7828 ± 235
2857	Ayton_raster3	Nodules at Mary Anning/Groken drill site	i	P	2.44 ± 0.05	5.49 ± 0.28	1.49 ± 0.02	16.27 ± 0.2	1505 ± 50
1686	Newport_Ledge	Coating	c, d	Fe, Zn	2.27 ± 0.05	0.79 ± 0.05	1.51 ± 0.06	31.02 ± 0.33	3994 ± 120
2857	Ayton_raster2	Nodules at Mary Anning/Groken drill site	i	P	1.91 ± 0.04	3.56 ± 0.19	1.53 ± 0.04	16.26 ± 0.2	1967 ± 60
2857	Ayton_raster1	Nodules at Mary Anning/Groken drill site	i	P	1.40 ± 0.04	2.67 ± 0.14	1.66 ± 0.04	16.97 ± 0.2	2296 ± 70
2906	Groken_DRT	Nodules at Mary Anning/Groken drill site		P	1.40 ± 0.04	2.64 ± 0.14	1.73 ± 0.03	16.43 ± 0.20	2175 ± 70
2450	Badcall	Possible nodules		Zn	1.25 ± 0.04	1.19 ± 0.07	0.96 ± 0.04	20.69 ± 0.26	4465 ± 135
2908	Trow_offset	Nodules at Mary Anning/Groken drill site	i	P	1.24 ± 0.03	2.49 ± 0.14	1.61 ± 0.04	16.14 ± 0.20	2171 ± 70
1679	Maple_Spring	Nodules		P	1.21 ± 0.04	2.97 ± 0.16	1.36 ± 0.06	17.98 ± 0.2	1090 ± 40
2906	Groken_offset	Nodules at Mary Anning/Groken drill site		P	1.20 ± 0.03	2.22 ± 0.12	1.57 ± 0.04	15.18 ± 0.20	1924 ± 60
2908	Trow_DRT	Nodules at Mary Anning/Groken drill site	i	P	1.15 ± 0.03	2.38 ± 0.14	1.72 ± 0.03	16.19 ± 0.20	2072 ± 65
2906	Groken_tailings	Nodules		P	1.07 ± 0.03	2.13 ± 0.12	0.50 ± 0.02	19.66 ± 0.26	2118 ± 0.65
935	Alvord_Mountain_ raster1	Vein		Ca, Ge	1.04 ± 0.04	0.71 ± 0.07	1.69 ± 0.07	14.28 ± 0.2	2253 ± 70
2862	Falkirk_Wheel	Nodules at Mary Anning/Groken drill site		P	1.03 ± 0.03	2.01 ± 0.12	1.47 ± 0.03	18.32 ± 0.2	1950 ± 60

^aAll of the features are dark in images, relative to the surrounding bedrock.

^bSee Figure 3 for images.

Table S4: Evaporation modelling details and initial solution composition adapted from Snake River Plains Basalt Aquifers (SRPB)

Solute	Concentration (mg/L)	Reference	Comments
Adapted from Snake River Plains Basalt Aquifers (SRPB)			
Ca ²⁺	51	(Wood & Low, 1988) ^a	
Mg ²⁺	17	(Wood & Low, 1988)	
Na ⁺	43	(Wood & Low, 1988)	
K ⁺	5	(Wood & Low, 1988)	
HCO ₃ ⁻	0.1	Mean SRB (Wood & Low, 1988) is 222 mg/L	Lowered from 222 mg/L to suppress carbonate precipitation (Wood & Low, 1988) report 32 mg/L; (Newcomb, 1972) maintain that >30 mg/L is unusually high because it is elevated in shallow wells in semiarid basins where evaporite chlorides in soil and regolith probably contribute higher Cl ⁻
Cl ⁻	10 (Charge balance)	(Newcomb, 1972) ^b	Average sulfate for CRBG is lower: 20 mg/L (Newcomb, 1972) ^b
SO ₄ ²⁻	67	(Wood & Low, 1988)	
SiO ₂	37	(Wood & Low, 1988)	
Fe ²⁺	0.040	(Wood & Low, 1988)	Median of analyses above detection limit 10 µm/L (63% of total analyses). Consistent with (Steinkampf & Hearn, 1996) ^c mean of 51 µg/L
Mn ²⁺	0.010	(Wood & Low, 1988)	Median of analyses above detection limit stated as both 10 µm/L and 1 µm/L (57% of total analyses). Consistent with (Steinkampf & Hearn, 1996) ^c mean of 15 µg/L
HPO ₄ ²⁻	0.13	(Newcomb, 1972)	"Common range" reported is 0.02 to 0.30 mg/L in CRBG

^aWood and Low (1988) Table 4 concentrations are from 230 wells and springs representative of the Snake River Plain regional aquifer system.

^bNewcomb (1972) covered a much larger study area than Wood and Low (1988): most of the Columbia River Basalt Group (CRBG) in Oregon, Washington, and Idaho.

^c(Steinkampf & Hearn, 1996) compiled analyses from wells in Grande Ronde Basalt unit (GRBu) of the Columbia River Basalt Group (CRBG) (summer 1982 through spring 1984).

Table S5: Modelled parameters for initial and final evaporated solutions^a

Step	Ionic strength (molal)	Dissolved solids (mg/kg sol'n)	pH	Eh (V)	pe	Log fO ₂	Activity of H ₂ O	Solution mass (kg)	Chlorinity (molal)	Water type	Fluid volume (cm ³)	Mineral volume (cm ³)
Adapted from Snake River Plains Basalt Aquifers (SRPB)												
Initial input after charge rebalancing (Cl)	0.00817	382	7.40	0.0723	1.2214	-48.62	0.9998	1	0.0046	Ca-Cl	1000	0
Evaporated solution (0.1% of initial water remaining)	4.17	2x10 ⁵	5.96	0.2205	3.7275	-44.44	0.8987	1.2x10 ⁻³	4.7	Na-Cl	1.07	0.066

^aModel calculated with Geochemist's Workbench and thermo.tdat database. Temperature: 25°C. Suppressed minerals: SiO₂ polymorphs quartz, cristobalite, and tridymite because amorphous SiO₂ is most likely to precipitate first (e.g., Drever, 1997); hematite because goethite is observed to precipitate first at low temperatures (e.g., Langmuir & Whittemore, 1971). Minerals allowed to back-react with solution.

Table S6: Description of sample preparation methods

Preparation method	Abbreviation (Data Set S1)	Description
Unbrushed rock	RU	As-is, unbrushed rock surface
Brushed rock	RB	Rock surface after brushing by DRT
Minidrill	MD	Shallow test drill; ~2-5 mm in depth; APXS deployed over chipped/abraded rock
Drill tailings	DT	Drill tailings ejected from the hole without being acquired by SA/SPaH, extracted from a range of depths in the drill hole up to ~5 cm and primarily from the top 2-3 cm
DBA drill fines	DBA	Sample dumped from the drill bit assembly (DBA) using the feed extended drilling and feed extended sample transfer (FED/FEST) techniques (sols >1536)
Sieved < 150 μm	Postsieve	Sample processed by SA/SPaH, sieved to <150 μm , and dumped on the ground. The targets include "postsieve" in the name
Sieved >150 μm	Presieve	Sample processed by SA/SPaH that did not pass through the 150 μm sieve, and dumped on the ground. The targets include "presieve" in the name
Sieved 150-1000 μm	Sieve150 μm -1mm	Sample processed by SA/SPaH, sieved to 150-1000 μm , and dumped on the ground.
Sieved >1000 μm	Sieve1mm	Sample processed by SA/SPaH, sieved to >1000 μm , and dumped on the ground
Undisturbed soil/sand	SU	Soil and sand as-is, untouched by the rover hardware
Disturbed soil/sand	SD	Soil and sand that has been disturbed by the rover's scoop and/or wheels
Failed drill fines	Failed	Sample fines dumped by SA/SPaH but did not fill the APXS FOV and/or was not infinitely thick with respect to APXS sampling depth

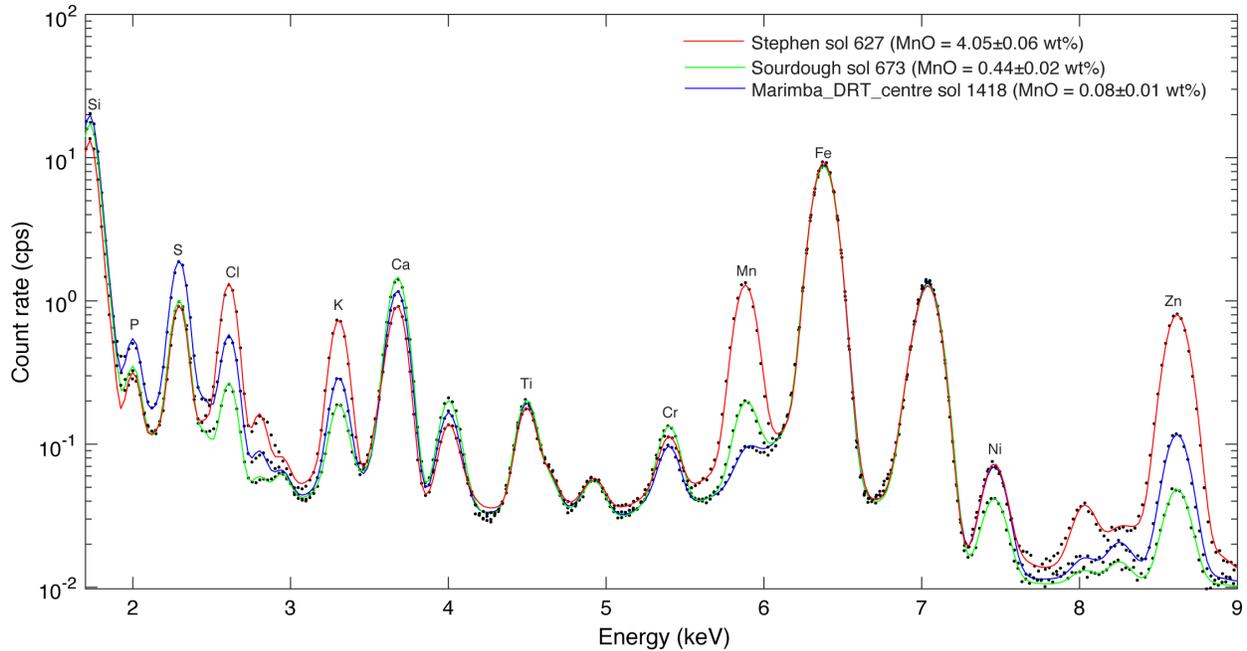


Figure S1: Representative APXS spectra showing the range of Mn concentrations found by the APXS in Gale crater. The three measurements shown had similar standoff (within 2 mm of the surface), integration time (~8 h), and ideal FWHM (147-152 eV; Fe K_{α}). The target names and corresponding MnO concentrations are included in the legend. The spectra demonstrate that low concentrations of MnO (≥ 0.05 wt%) are quantifiable. In particular, the large Fe K_{α} peak does not preclude Mn quantification in samples with high FeO content (~20 wt%). For clarity, the full spectra (0.8 – 25 keV) are not shown; rather an energy range focusing on the elements highlighted in the manuscript (P, Cl, Mn, Fe, and Zn) was chosen. Selected K_{α} peaks are denoted, and unlabeled peaks include the K_{β} lines of Cl, Ca, Ti, Fe and Ni as well as the Ar K_{α} peak, sourced from the atmosphere. Dots capture the observed Mars spectra and lines represent an analytical model (i.e., fit of the data) used to derive the composition of these targets.

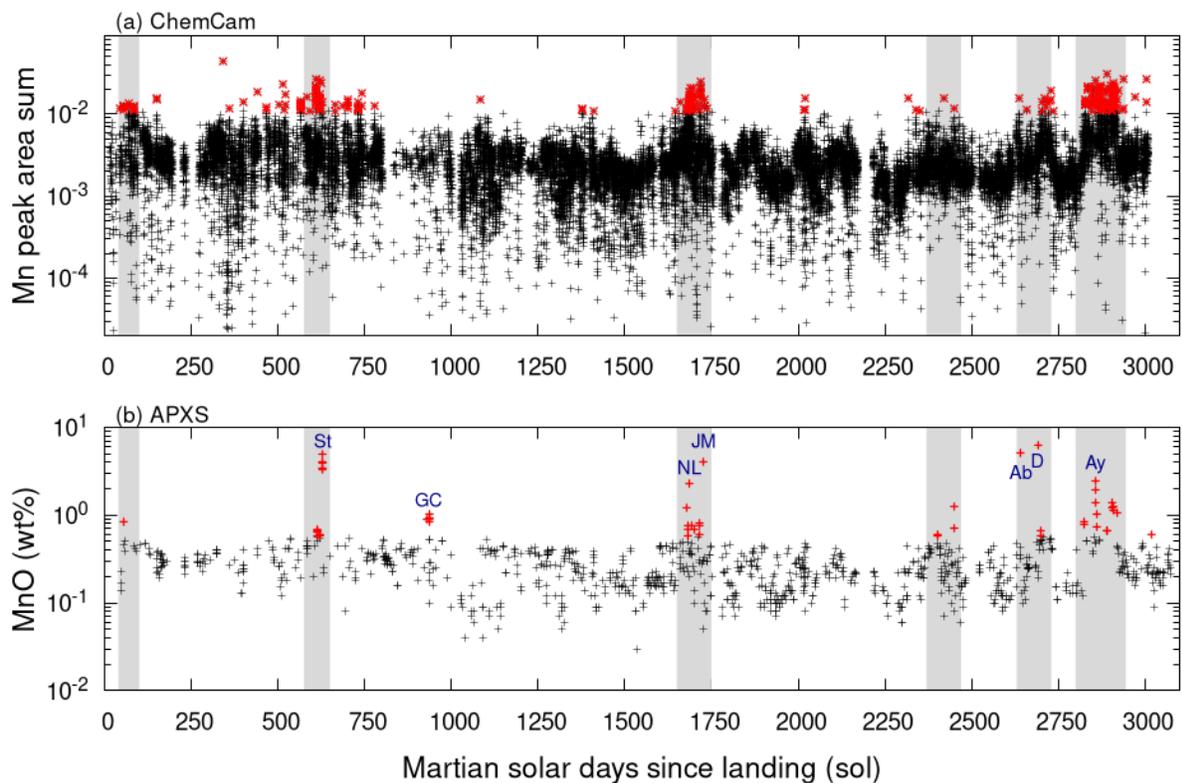


Figure S2: Comparison of ChemCam and APXS results showing the occurrence of high-Mn targets along Curiosity's traverse. (a) ChemCam Mn peak areas plotted versus sol (0-3068), with targets in the top 1% of Mn peak areas highlighted with a red 'x' ($n = 248$). The peak areas were determined from the median spectrum of shots 5-30, normalized to the intensity of the relevant spectrometer ("Norm3"). The area was determined by a summation of the triplet peaks in the 403-404nm range (Lanza et al., 2014, 2016) after a linear background removal. (b) APXS MnO concentrations versus sol with targets in the top 5% of MnO concentrations denoted by a red 'x' ($n = 50$). Regions with clusters of high Mn ChemCam targets correlate qualitatively with regions where high Mn targets were found by the APXS (indicated by shaded boxes). Data are from the PDS Geosciences node: APXS has the DOI 10.17189/1518757 and the ChemCam archive is <https://pds-geosciences.wustl.edu/missions/msl/chemcam.htm>.

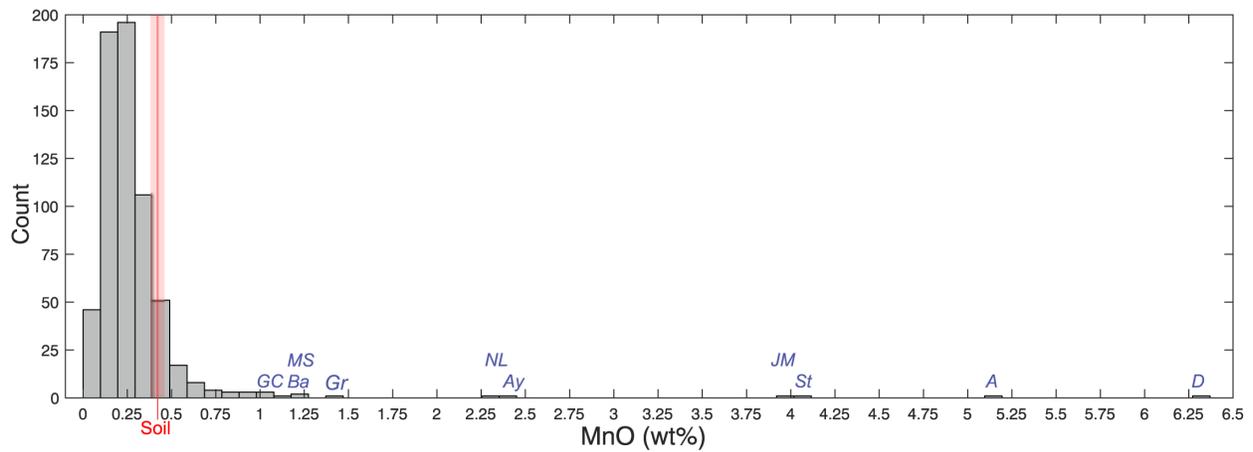


Figure S3: Histogram of MnO concentrations for the 638 APXS targets discussed in the text. The histogram has 65 bins with a width of 0.1 wt%. The nine targets with MnO concentrations >1 wt% are denoted: Garden City (GC), Maple Spring (MS), Badcall (Ba), Groken (Gr), Newport Ledge (NL), Ayton (Ay), Jones Marsh (JM), Stephen (St), Abernethy (A), and Dunbartonshire (D). The mean soil concentration (0.42 ± 0.04 wt%) is indicated in red.

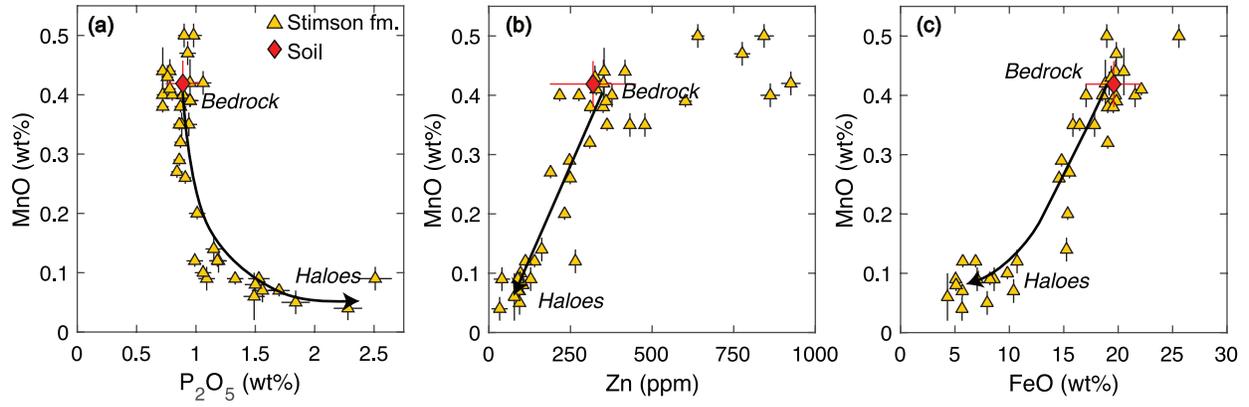


Figure S4: MnO versus (a) P₂O₅, (b) Zn, and (c) FeO in the Stimson formation sandstone and fracture-associated haloes. The silica-rich haloes (arrows) are enriched in P and depleted in Zn and Fe relative to the bedrock.

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