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

Jeff A Berger¹, Penelope King², Ralf Gellert³, Benton C. Clark⁴, Victoria A Flood⁵, Michael A. McCraig³, Douglas Ming¹, Catherine D O'Connell-Cooper⁶, Mariek E. Schmidt⁷, Lucy M Thompson⁶, Scott J VanBommel⁸, Brent Wilhelm³, and Albert S. Yen⁹

¹NASA Johnson Space Center
²Australian National University
³University of Guelph
⁴Space Science Institute
⁵University of Toronto
⁶University of New Brunswick
⁷Brock University
⁸Washington University in St. Louis
⁹Jet Propulsion Lab (NASA)

November 24, 2022

Abstract

In Gale crater on Mars, the rover *Curiosity* has discovered evidence of fluid mobilization of the redox-sensitive element manganese. We present results for Mn from *Curiosity*'s Alpha Particle X-ray Spectrometer (APXS), which show that the average MnO concentration in mudstone-dominated sedimentary units (0.22 wt%) is about one-half of the concentration in the average Mars crust (0.44 wt%). Geochemical trends indicate that Mn in the sedimentary bedrock, most of which has a basaltic provenance, was leached by chemical alteration and dissolution. In >350 vertical meters of mudstone-dominated strata, the apparent leaching of Mn and retention of Fe in Fe-O-H phase(s) resulted in the fractionation of Fe and Mn, indicating relatively moderate Eh-pH fluid conditions that were not highly alkaline, reducing, or oxidizing. Exceptions are fracture-associated, silica-rich haloes where both Mn and Fe were leached by low pH fluids. The rover also discovered Mn-rich veins, nodules, and patchy, dark coatings on rock surfaces, which are variably associated with enrichments in Fe, P, Cl, and/or Zn. These Mn-rich features represent ~1% of the 1,029 APXS measurements acquired over ~25 km of rover traverse. A thermochemical model shows that dissolved Mn²⁺ could have been concentrated via evaporation, sublimation, and/or freezing. Manganese was then likely precipitated in localized features when > 99.99% of the Mn²⁺-bearing water was removed from the system. These findings indicate that Mn was mobile in Gale crater and therefore bioavailable as a potential energy source for life.

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

- 2 J. A. Berger^{1*}, P. L. King², R. Gellert³, B. C. Clark⁴, V. A. Flood⁵, M. A. McCraig³, D. W. Ming¹,
- 3 C. D. O'Connell-Cooper⁶, M. E. Schmidt⁷, L. M. Thompson⁶, S. J. V. VanBommel⁸, B. Wilhelm³,
- 4 A. S. Yen⁹.
- 5
- 6 ¹NASA Johnson Space Center
- 7 ²Research School of Earth Sciences, The Australian National University, Canberra, AUS
- 8 ³University of Guelph, Guelph, CAN
- ⁹ ⁴Space Science Institute, Boulder, CO, USA
- 10 ⁵University of Toronto, Toronto, CAN
- 11 ⁶University of New Brunswick, Fredericton, CAN
- 12 ⁷Brock University, St. Catharines, CAN
- 13 ⁸Washington University, St. Louis, USA
- ⁹JPL-Caltech, Pasadena, USA
- 15 *Corresponding author jeffrey.a.berger@nasa.gov
- 16
- 17 Key Points
- In Gale crater on Mars, manganese is depleted in bedrock and enriched in nodules, veins, and coatings
- Manganese was likely leached by aqueous chemical alteration and concentrated via evaporative brine evolution and diagenesis
- Manganese and iron fractionation in mudstone counter-indicates highly alkaline, reducing,
 and/or oxidizing fluid conditions

24 Plain language summary

25 In Gale crater on Mars, the rover Curiosity has discovered evidence of the mobility of the 26 redox-sensitive element manganese. We present results for manganese analyses from *Curiosity*'s 27 Alpha Particle X-ray Spectrometer (APXS), an instrument that measures the elemental 28 compositions of martian materials. In most of the layered sedimentary bedrock, manganese 29 concentrations are about one-half of the average Mars crustal composition (approximated as 30 basaltic soil). Our interpretation of the manganese-depleted bedrock is that the element was 31 leached by chemical processes involving water. In most of the bedrock, manganese was likely 32 removed in fluids, whereas iron was not, indicating that this occurred under relatively moderate 33 aqueous conditions. The rover has also discovered manganese-rich veins, nodules, and dark 34 coatings on rock surfaces. These manganese-rich features are associated with enrichments in iron, 35 phosphorus, chlorine, and/or zinc. We provide a thermochemical model to support the hypothesis 36 that the reduced form of manganese (Mn²⁺) could have been dissolved in water and concentrated as the water evaporated. Manganese was then deposited in localized features when > 99.99% of 37 38 the Mn²⁺-bearing water was removed by evaporation. These findings indicate that manganese was 39 dissolved in Gale crater water and was accessible as a potential chemical energy source for life.

40 Abstract

41 In Gale crater on Mars, the rover *Curiosity* has discovered evidence of fluid mobilization of 42 the redox-sensitive element manganese. We present results for Mn from Curiosity's Alpha Particle 43 X-ray Spectrometer (APXS), which show that the average MnO concentration in mudstone-44 dominated sedimentary units (0.22 wt%) is about one-half of the concentration in the average Mars 45 crust (0.44 wt%). Geochemical trends indicate that Mn in the sedimentary bedrock, most of which 46 has a basaltic provenance, was leached by chemical alteration and dissolution. In >350 vertical 47 meters of mudstone-dominated strata, the apparent leaching of Mn and retention of Fe in Fe-O-H 48 phase(s) resulted in the fractionation of Fe and Mn, indicating relatively moderate Eh-pH fluid 49 conditions that were not highly alkaline, reducing, or oxidizing. Exceptions are fracture-associated, 50 silica-rich haloes where both Mn and Fe were leached by low pH fluids. The rover also discovered 51 Mn-rich veins, nodules, and patchy, dark coatings on rock surfaces, which are variably associated 52 with enrichments in Fe, P, Cl, and/or Zn. These Mn-rich features represent ~1% of the 1,029 APXS 53 measurements acquired over ~25 km of rover traverse. A thermochemical model shows that

Confidential manuscript for JGR-Planets

54 dissolved Mn^{2+} could have been concentrated via evaporation, sublimation, and/or freezing. 55 Manganese was then likely precipitated in localized features when > 99.99% of the Mn^{2+} -bearing 56 water was removed from the system. These findings indicate that Mn was mobile in Gale crater 57 and therefore bioavailable as a potential energy source for life.

58 1. Introduction

59 The Mars Science Laboratory (MSL) rover, Curiosity, has discovered localized manganese enrichments in the sedimentary rocks of Gale crater with the Alpha Particle X-ray Spectrometer 60 61 (APXS) and ChemCam geochemical instruments (Berger et al., 2020; Lanza et al., 2014, 2016; 62 Thompson et al., 2016, 2020). APXS measurements show that most of the bedrock, however, is 63 lower in Mn by roughly a factor of two compared to the average martian crust (Taylor & McLennan, 2010). Sedimentological, geochemical, and mineralogical evidence in Gale crater 64 65 indicates that the sediments were deposited in a fluvio-lacustrine system (e.g., Grotzinger et al., 2015; Rampe et al., 2017) where redox reactions may have influenced water chemistry (Hurowitz 66 67 et al., 2017). Manganese is a redox-sensitive element, and the pathway(s) by which it was 68 mobilized are likely recorded in the sedimentary rocks of Gale crater such that the geochemical 69 conditions in the crater can be constrained. Here, we present APXS results for the occurrence of 70 Mn in Gale crater and propose a pathway for Mn depletion in the bedrock and subsequent 71 enrichment via chemical alteration, concentration in fluids, and precipitation in localized features.

72 *Curiosity*'s >3100 martian solar day (sol; 24.7 h) traverse in Gale crater has been effectively a 73 transect of ~500 m of flat to gently dipping, bedded sedimentary strata (e.g., Edgar et al., 2020; 74 Grotzinger et al., 2015; Stein et al., 2020). Based primarily on sedimentological and orbital 75 observations, a composite stratigraphic column delineates three different sedimentary groups 76 wherein APXS measurements were acquired: Mount Sharp, Bradbury, and Siccar Point (Figure 1) (e.g., Edgar et al., 2020; Grotzinger et al., 2014, 2015). A simplified version of that stratigraphic 77 78 column is also apparent in plots of sol versus elemental concentrations from the APXS (Figure 2). 79 The lowermost Bradbury group has a lacustrine mudstone (Sheepbed member) that is overlain by 80 fluvial-alluvial sandstone and conglomerate (Grotzinger et al., 2014; Rice et al., 2017; Williams 81 et al., 2013). The Mount Sharp group contains the Murray and overlying Carolyn Shoemaker 82 formations, which are primarily laminated lacustrine mudstone with minor fluvial-aeolian

83 sandstone (e.g., Edgar et al., 2020; Grotzinger et al., 2015). The rover's traverse from sol ~2300-84 3076 was in the informally-named Glen Torridon region, which bridges the Murray and Carolyn 85 Shoemaker formations and is denoted separately herein because Glen Torridon was predicted to 86 be a distinct phyllosilicate-bearing assemblage based on orbital data (Milliken et al., 2010). A 87 capping unit, the Siccar Point group, is primarily a cross-bedded aeolian sandstone that 88 unconformably overlies the Murray formation and Glen Torridon region (S. G. Banham et al., 89 2018, 2021). The ancient aqueous depositional environments evident in Gale crater are reflected 90 in the compositions of the sedimentary materials because several lines of evidence indicate that 91 elements were mobile in Gale crater fluids (e.g., Berger et al., 2020; Rampe et al., 2017; Thompson 92 et al., 2016, 2020; Yen et al., 2017, 2021). Manganese is among the elements with evidence of 93 mobilization in Gale crater fluids, and this has the potential to constrain ancient geochemical 94 conditions.

95 2. Methods

96 The APXS instrument analyzes elemental abundances in geologic samples using a combination 97 of particle-induced X-ray emission spectrometry (PIXE) and X-ray fluorescence (XRF) techniques 98 (Campbell et al., 2012; Gellert et al., 2006, 2009). The arm-mounted instrument is deployed by 99 the rover to within ~ 2 cm of the target surface. We define "target" as a spot on the surface of a 100 sample that is usually < 4 cm in diameter and is given a name and the coordinates presented in 101 Data Set S1. Radiation emitted from curium-244 radioisotope sources induces characteristic X-102 rays in the ~2-cm-diameter sampling area, which are counted with a detector and converted into 103 an energy dispersive X-ray spectrum. Major, minor, and selected trace element concentrations for 104 atomic number $Z \ge 11$ are calculated from the relative counts in characteristic X-ray peaks, which 105 correlate to the relative abundance of elements in the specimen (Figure S1). Errors reported here 106 represent uncertainty in precision (2σ) and other instrument effects. Instrument accuracy and 107 typical precision error is shown in Table S1 (Gellert & Clark, 2015). The APXS detection limit for 108 MnO is 500 μ g/g (ppm) under typical measurement conditions. Sixteen oxides and elements are 109 reported after assigning oxygen to cations and normalizing to 100 weight percent (wt%). Oxidation 110 state is not measured by the APXS; by convention, sulfur, chlorine, manganese, and iron are 111 reported in weight percent respectively as SO₃, Cl, MnO, and FeO. Considerations such as target preparation (e.g., brushing, drilling) and measurement conditions (e.g., standoff distance,
temperature, duration) are discussed in detail by Berger et al. (2020) and VanBommel et al. (2019).

114 Of~1000 total APXS measurements acquired over ~3000 sols (Figure 1; Data Set S1), 200 are 115 omitted from the plots and mean calculations because they are either (1) low quality due to substandard statistics or spectral resolution (FWHM Fe $K_{\alpha} > 210$ eV), (2) have a visible mixture of 116 117 different materials in the APXS field of view (e.g., Ca-sulfate veins crosscutting silicate bedrock), (3) float (i.e., loose fragments of rock with an indeterminate geologic context having compositions 118 119 distinct from local bedrock), and/or (4) wind-blown deposits of loose, unconsolidated materials. 120 Of the 1028 APXS measurements, 269 are effectively duplicate measurements of the same target. 121 Multiple measurements of one target are conducted to investigate chemical heterogeneity on the 122 surface (typically over a distance of 1-3 cm) or within fines drilled from depths of up to 5 cm 123 (Berger et al., 2020). APXS rasters are also conducted to deconvolve features that are small with 124 respect to the ~2 cm APXS field of view (VanBommel et al., 2016). The duplicate measurements 125 are included and denoted in Data Set S1 but are not plotted in figures herein because they 126 misrepresent the frequency and distribution of targets; that is, small features such as veins and 127 nodules are often rastered, and the additional measurements do not represent multiple targets with 128 that composition. After the described measurements were omitted, 638 of 1028 are shown in the 129 figures. Mean elemental concentrations in bedrock were calculated with the same omissions, and 130 measurements of diagenetic features (e.g., nodules and veins) were also omitted from mean 131 calculations. All APXS measurements up to sol 3076 are included in Data Set S1.

We consider basaltic soil as an approximation of the average martian crust because analyses from two Viking lander sites and APXS results from four rover sites show that it has a relatively uniform chemical composition (B. C. Clark et al., 1982; Foley et al., 2003; Ming et al., 2008; O'Connell-Cooper et al., 2017; Yen et al., 2005). Herein, we describe elemental concentrations relative to the 12 basaltic soil targets measured in Gale crater (stratigraphic group "soil" in Data Set S1). The soils are distinguished chemically by (1) a molar S/Cl ratio of 3.3 ± 0.2 , (2) mean MnO concentration of 0.42 ± 0.04 wt%, and (3) a molar Fe/Mn ratio of 46 ± 2 .

139 **3.** Results

140 Curiosity's APXS instrument acquired 1028 measurements of geologic targets along the rover's traverse during sols 0-3076 (Figure 1). The rover's traverse has largely been upsection 141 142 through a sequence of more or less flat-lying sedimentary strata (e.g., Banham et al., 2018; Edgar 143 et al., 2020; Fedo et al., 2018; Grotzinger et al., 2014, 2015; Stack et al., 2019). Thus, plots of 144 elemental concentrations versus sol provide an approximate chemical profile through the strata of 145 the Bradbury, lower Mt. Sharp (Murray formation and Glen Torridon), and Siccar Point groups 146 (Figure 2). Mean concentrations and $\pm 2\sigma$ are reported for bedrock units and exclude 10 targets with MnO >1 wt%. The APXS results are presented with operating parameters, sample comments, 147 148 and geologic context in Data Set S1 with an explanation in the supplementary information. In this 149 section, we first discuss the occurrence of Mn in Gale crater using APXS results, and then we 150 discuss the occurrence Cl, P, Zn, and Fe enrichments that are associated with Mn-rich features.

151 **3.1. Manganese occurrence**

The three main stratigraphic groups explored by *Curiosity* (Bradbury, Mt. Sharp, and Siccar Point) have distinct ranges in bulk elemental compositions (Berger et al., 2020; Thompson et al., 2016, 2020). The Mn occurrence in the bedrock is also distinct between each sedimentary group, as summarized below and in Figure 2a.

156 Bradbury Group bedrock: The Bradbury group can be described by three compositional 157 endmembers: basaltic, potassic basalt, and high total alkali (> 5 wt% Na₂O + K_2O) (Berger et al., 158 2020; Thompson et al., 2016; Treiman et al., 2016). The lowermost unit of the Bradbury group, 159 the basaltic Sheepbed mudstone at Yellowknife Bay (McLennan et al., 2013; Vaniman et al., 160 2014), has lower MnO (0.30 ± 0.08 wt%). In contrast, the overlying basaltic and potassic basalt 161 sandstone and conglomerate contain MnO (0.40 ± 0.30 wt%) at concentrations similar to soil but 162 with larger variability. Fourteen mugearitic clasts, hypothesized to have relatively unaltered 163 igneous compositions, have lower MnO $(0.21 \pm 0.10 \text{ wt\%})$ than the basaltic materials (Schmidt et 164 al., 2014; Thompson et al., 2016).

Mt. Sharp Group bedrock: The Mt. Sharp group includes the Murray and Carolyn Shoemaker formations, and it comprises most of *Curiosity*'s traverse from sols 720-3076. The Glen Torridon region (sols 2301-present; Figure 1) contains parts of the Murray and Carolyn Shoemaker

168 formations, as detailed in Data Set S1. Because preliminary interpretations of Glen Torridon 169 indicate a changing depositional environment possibly related to the overlying sulfate-bearing unit 170 (Milliken et al., 2010), we highlight the Glen Torridon results (sols 2302-3076) separately from 171 the other Mt. Sharp results (sols 720-2301). In the Murray formation and Glen Torridon region, 172 the bulk elemental composition of the bedrock is depleted in Ca and Mg, and enriched in Si, 173 relative to basaltic soil. MnO is consistently depleted $(0.22 \pm 0.20 \text{ wt\%})$ when the Mn-rich nodular, 174 vein, and coating measurements are excluded (MnO > 0.75 wt%). A high-SiO₂ (58-74 wt%) facies 175 typified by the Buckskin target occurs in the Murray formation and has very low MnO (< 0.08 176 wt%).

177 Siccar Point Group bedrock: The Stimson formation of the Siccar Point group unconformably 178 overlies the Murray formation (Banham et al., 2018) and has a basaltic, soil-like major element 179 composition (Yen et al., 2017). Similarly, MnO concentrations in the bedrock is soil-like, but with 180 greater variability $(0.40 \pm 0.21 \text{ wt}\%)$.

Light-toned alteration haloes (~50 cm wide) are associated with fractures and crosscut the Stimson and Murray formations (Yen et al., 2017) and possibly the Bradbury group (Gabriel et al., 2019). The haloes are depleted in MnO, with concentrations as low as 0.05 wt% (Yen et al., 2017). Haloes are also depleted in Al, Fe, Mg, Zn, Ni, and enriched in Si, Ti, P, and Ca-sulfate (Yen et al., 2017).

186 Manganese enrichments are limited on Curiosity's traverse and occur in a variety of localized 187 mm-cm scale features that are not a major component of the Gale crater bedrock (Figures 2, 3; 188 Data Set S1; Table S3). Concentrations of MnO are greater than soil $(0.42 \pm 0.04 \text{ wt\%})$ in ~10% 189 of targets, and 12 targets have >1 wt% MnO (Figure S3; Table S3). The Mn-enriched features 190 occur as: (1) veins that crosscut bedrock and are less than 5 cm wide (e.g., Alvord Mountain, 191 Abernethy, Dunbartonshire; Figure 3g, 3h); (2) nodules in bedrock (e.g., Timber Point, Ayton, 192 Groken, Falkirk Wheel; Figure 3i); (3) smooth coatings on rock surfaces (e.g., Stephen, Newport 193 Ledge; Figure 3a, 3b, 3c, 3d); and (4) patchy coatings on rock surfaces (e.g., Jones Marsh; Figure 194 3e, 3f). All of these features are dark-toned relative to adjacent bedrock, which is particularly 195 apparent after the ChemCam LIBS instrument interacted with the surfaces and removed dust. 196 Examples representative of the different enriched features are presented in Figure 3, and 197 summaries of the measurements with MnO >1 wt% are given in Table S3. Only one nodular Mn-

Confidential manuscript for JGR-Planets

rich target (Groken) was drilled and delivered to CheMin and SAM because the features are typically too small with respect to *Curiosity*'s drill volume and/or could have broken under the force of the drill. Groken results are currently being prepared for publication and preliminary data have been presented (Berger et al., 2021; J. V. Clark et al., 2021; Lanza et al., 2021; Thorpe et al., 202 2021; Treiman et al., 2021).

203 Because most of the Mn-rich features are small with respect to the APXS ~2 cm field of view, 204 the APXS measurements are typically a mixture of the enriched feature as well as the host bedrock 205 and/or other adjacent phases. For example, the raster of the dark, Mn-, Ca-, and Ge-rich Alvord 206 Mountain vein contains high concentrations of SO₃ (up to 40 wt%) because the vein is a mix of 207 different amounts two phases that both were contained in the APXS field of view: (1) dark Mn-208 rich material and (2) white Ca-sulfate (Berger et al., 2017; VanBommel et al., 2017). As a result, 209 many of the APXS measurements of Mn-rich features are not exactly representative of the feature 210 alone and are minimum concentrations.

211 The ChemCam instrument, a laser induced breakdown spectrometer (LIBS) on the rover's mast 212 (Wiens et al., 2013), has also detected Mn enrichments (Lanza et al., 2014, 2016; Gasda et al., 213 2018). In general, the stratigraphic locations where Mn enrichments were found by ChemCam 214 correspond with those found by the APXS (Figure S2) (Lanza et al., 2014, 2016; Gasda et al., 215 2018). Some of the Mn-rich targets were analyzed by both the APXS and ChemCam instruments 216 (e.g., Stephen, Newport Ledge) (Lanza et al., 2016). A larger number of localized Mn enrichments 217 were found by ChemCam than by the APXS, which is likely due to two considerations. First, 218 ChemCam has probed 3-4 times more unique targets than the APXS, and ChemCam has been 219 used to investigate a larger number of heterogenous features than the APXS (e.g., Nachon et al., 220 2014, 2017). Second, ChemCam shots are ~350 µm in diameter and progressively ablate material with typically ~30 LIBS shots per spot, whereas the APXS FOV is ~2 cm in diameter and the 221 222 sampling depth increases with atomic number Z from ~3 µm (Na) to ~90 µm (Fe) (e.g., Schmidt 223 et al., 2018). ChemCam is therefore more likely to detect sub-mm enrichments that may not be 224 readily identifiable in standard analyses of APXS data due to the difference in sampling volume 225 (e.g., L'Haridon et al., 2020). Because the sampling volume of ChemCam and APXS is 226 significantly different, we do not make direct comparisons here. In addition, several elemental 227 correlations we discuss in this work (S, Cl, P, Zn) are not possible to evaluate using ChemCam

data due to significantly higher detection limits and accuracy uncertainty (e.g., Forni et al., 2015;
Lasue et al., 2016; Wiens et al., 2013).

230 **3.2.** Other elemental characteristics of manganese-rich features

231 Manganese enrichments are commonly accompanied by high concentrations of Cl, P, Zn 232 and/or Fe, which are elements that were also mobile in Gale crater because high concentrations 233 are often associated with veins, nodules, and coatings interpreted to be diagenetic (e.g., Berger et 234 al., 2017, 2020). There is abundant evidence of S mobility, particularly in the white Ca-sulfate 235 veins that crosscut nearly every unit, but there is no apparent correlation of S with Mn. The lack 236 of correlation between Mn and S is notable because rocks with very high MnO (~3.5 wt%) and 237 SO₃ (~35 wt%) were found by the rover *Opportunity* on the rim of Endeavor crater (Arvidson et 238 al., 2016). Below, we present results for Cl, P, Zn, and Fe, first giving an overview of bedrock 239 concentrations for each element, then summarizing enrichments that occur in Mn-rich features.

240 **3.2.1.** Chlorine

241 In the Gale crater bedrock, in general there is no clear correlation between Mn and Cl. Chlorine 242 varies $(1.27 \pm 0.94 \text{ wt}\%)$; Figure 2b), with the lowest concentration found in the Buckskin drill 243 fines $(0.28 \pm 0.01 \text{ wt})$. Drilled targets show that the top ~1 mm of the bedrock surface is enriched 244 in Cl: the median Cl concentration in drilled material from a few cm below the surface (0.56 wt%) 245 is about half of the median Cl concentration in unbrushed surfaces (1.23 wt%) and brushed surfaces 246 (1.06 wt%) (Berger et al., 2020). Evolved gas analyses (EGA) of drilled samples in the SAM 247 instrument indicate that a fraction of the Cl in the bedrock is within mixed oxychlorine species 248 (Mg-, Ca-, Na-, and/or K-chlorate or perchlorate) (Sutter et al., 2018). Chlorine-bearing phases 249 were detectable with CheMin XRD only as a minor amount of halite (1 wt%) in one of the Murray 250 formation mudstone samples (Quela) (Achilles et al., 2020). SAM and CheMin analyses cannot 251 account for the total Cl measured by the APXS, and a fraction of Cl likely is in the X-ray 252 amorphous fraction that comprises ~20-50 wt% of all drilled samples (Achilles et al., 2020; 253 Morrison et al., 2018; Sutter et al., 2018).

Notable Cl concentrations occur in some, but not all of the Mn-rich targets. Chlorine concentrations are very enriched in Stephen and Jones Marsh (3.1-3.4 wt%) and elevated in Abernethy and Dunbartonshire (1.8-2.0 wt%; Figure 3; Figure 4a, 4b). Stephen has been 257 interpreted to be the eroded remnant of a vein next to the potassic basalt sandstone Windjana

258 (Figure 3a, 3b) (Lanza et al., 2016). Jones Marsh is a patchy, ~2-mm-thick coating (or crust) on

259 the surface of Murray formation bedrock (Figure 3e, 3f). Abernethy and Dunbartonshire have

260 similar morphologies consistent with erosion-resistant veins (Figure 3g, 3h). All four of these Mn-

and Cl-rich targets also have enrichment in either P, Zn, or Fe as described below.

262 **3.2.2.** Phosphorus

263 In the bedrock, P₂O₅ ranges from 0.48 to 2.5 wt% with a soil-like mean concentration of 0.95 ± 0.58 wt% and there are no clear correlations between Mn and P (Figure 2c; Figure 4c, 4d). Minor 264 265 amounts of fluorapatite (<4 wt%) were identified by CheMin in eight mudstone and sandstone 266 samples (Achilles et al., 2020; Rampe et al., 2017; Yen et al., 2017). In samples with fluorapatite, 267 not all of the P is accounted for in the crystalline phase and a fraction is thus associated with the 268 X-ray amorphous material, as it is in other drilled samples (Rampe et al., 2020). One exception 269 where Mn and P are negatively correlated is in fracture-associated alteration haloes in the cross-270 bedded Stimson sandstone (Figure S4). The Si-rich haloes are depleted in MnO by up to 90% and 271 enriched in P₂O₅ by up to 65% relative to the host bedrock. No crystalline P-bearing phases were 272 detected in drilled samples of two haloes by CheMin, thus the P is probably associated with the X-273 ray amorphous material in the haloes (Yen et al., 2017).

274 Seven of the 12 targets with enriched Mn (> 1 wt%; Table S3) have P enrichments (Figure 4c). Jones Marsh, which also has high Cl (3.10 ± 0.09 wt%), also has a notable P₂O₅ concentration of 275 276 7.56 ± 0.40 wt%. Phosphorus-rich features with elevated Mn that have been discovered by the 277 APXS are limited to two locations on Curiosity's traverse: (1) the vicinity of the Sutton 278 Island/Blunt's Point member contact within a ~500 m segment of the traverse (Cliffside Bridge, 279 Timber Point, Berry Cove, Maple Spring, and Jones Marsh) and (2) the Mary Anning and Groken 280 drill site in the Glen Torridon region (Ayton, Falkirk Wheel, Trow, and Groken). The latter four 281 targets are all dark nodules within a $\sim 1 \text{ m}^2$ area where the nodule-bearing Groken target was drilled.

282 **3.2.3. Zinc**

Zinc varies widely in the Gale crater bedrock, but it is consistently enriched over most of the traverse in the Bradbury and Mount Sharp groups $(1300 \pm 700 \text{ ppm})$ compared to soil $(300 \pm 50 \text{ ppm})$; Figure 2d, 4e, 4f) (Berger et al., 2017). There are three instances where Mn and Zn correlate: (1) In the Pahrump Hills member of the Murray formation, Mn and Zn correlate negatively with
increasing elevation in the laminated mudstone (sols 750-850) (Rampe et al., 2017). (2) Mn and
Zn are depleted in fracture-associated haloes, relative to adjacent less-altered bedrock, in the
basaltic sandstone of the Stimson formation (Figure S4). (3) Mn and Zn correlate with elevation
over two intervals on the traverse, first increasing and then decreasing (sols 1578-1850 and 23002520). Drilled samples analyzed by SAM and CheMin have not revealed any additional
information on what phase(s) may contain Zn.

Two Mn-rich targets have high Zn: Stephen (8000 ppm) and Newport Ledge (4000 ppm) (Figure 4e, 4f). The two targets both have dark surfaces but different morphologies (Figure 3b, 3d) and occur within very different local bedrock compositions. Stephen is next to the potassic basalt sandstone at the Windjana drill site (Treiman et al., 2016), and has been interpreted to be the fragment of a vein (Lanza et al., 2016), whereas Newport Ledge appears to be a smooth, thin coating on Murray formation sandstone.

299 **3.2.4.** Iron

300 Iron and manganese are not correlated in the Gale crater sedimentary bedrock (Figure 4g, 5a), 301 with two exceptions described below. The basaltic Stimson formation sandstone has soil-like FeO 302 concentrations (19.18 \pm 4.6 wt%) and molar Fe/Mn (49 \pm 10) (Yen et al., 2017). The Fe/Mn ratio 303 of the soil and Stimson sandstone is approximately the same as that determined for the average 304 martian crust (Taylor & McLennan, 2010) and bulk SNC martian meteorites (Figure 6). The soil-305 like Fe/Mn value is not shared by the Sheepbed mudstone, Murray formation, or Glen Torridon 306 region (Figure 2e, 5a, 5b), which have respective mean Fe/Mn values of 70, 100, and 110 primarily 307 due to depletion of Mn relative to Fe. Exceptions where FeO and MnO correlate positively are: (1) 308 the Stimson formation fracture-associated haloes, which have lower FeO and MnO due to the 309 apparent leaching of elements during low pH alteration (Yen et al., 2017), resulting in elevated 310 Fe/Mn (Figure 5) and (2) the high-SiO₂ facies of the Pahrump Hills member of the Murray 311 formation that has low FeO and MnO (Buckskin; Figure 5), possibly due to physical dilution by 312 high-silica volcanic detritus (Morris et al., 2016) and/or in situ leaching by fluids (Yen et al., 2021). 313 As a major element in every APXS analysis in Gale crater, FeO is contained within multiple 314 phases, including olivine, pyroxene, magnetite, hematite, jarosite, akaganeite, and the X-rav 315 amorphous material (e.g., Rampe et al., 2020).

Confidential manuscript for JGR-Planets

The association of Mn and Fe in Mn-rich features varies. Several targets enriched in MnO also have elevated FeO (Newport Ledge, Abernethy, and Dunbartonshire; Figures 2d, 3d, 3h, 4h). However, ~10 targets with notably enriched FeO (>25 wt%; e.g., Morancy Stream, Paradise Hill) have no corresponding MnO enrichment. Conversely, ~10 targets have enriched MnO (0.5-4.0 wt%) but do not contain elevated FeO concentrations; FeO is roughly the same as the bedrock in low-Fe, Mn-rich targets (e.g., Jones Marsh).

322 4. Discussion

323 Three key observations emerge from the results presented above:

- 324 (1) Most bedrock APXS targets (80%) have Mn concentrations below the average martian 325 crust (0.42 ± 0.04 wt%), and the median Gale crater bedrock (0.23 wt%) is half that of the 326 basaltic Gale crater soil.
- 327 (2) A small fraction of all APXS targets are enriched in Mn: ($\sim 10\%$) have MnO concentrations 328 above the range of soil (0.42 ± 0.04 wt%) and $\sim 1\%$ have MnO concentrations >1 wt%. The 329 highest concentrations of Mn are found in nodules, veins, and coatings.
- (3) Manganese-enriched targets have one or more enrichments in Fe, P, Cl, and/or Zn, even
 though these elements comprise a wide range of geochemical characteristics (e.g., ionic
 charge, solubility, and mineral affinity). There is compelling evidence that all of these
 elements were variably mobilized by fluids in Gale crater (e.g., Berger et al., 2020).

Below we propose a model that seeks to tie together these three observations, whereby Mn in the bedrock was depleted by chemical alteration of olivine and pyroxene, concentrated in brines via evaporation, sublimation, and/or freezing, and then ultimately precipitated at high concentrations in veins, nodules, and coatings.

338 4.1. Mn-depleted bedrock

Our interpretation is that the low MnO in the mudstone-dominated sedimentary units is the result of open-system chemical alteration and leaching of Mn from a basaltic precursor. Our reasoning is based on (1) the deduced provenance and (2) the altered characteristics of the rocks, as discussed below.

343 4.1.1. Bedrock provenance and primary Mn concentrations

344 The exact provenance of the sediments in Gale crater is unknown, so the Mn content of the protolith(s) is uncertain. However, APXS results provide evidence of bulk chemical similarities 345 346 between basaltic soil and the mudstone-dominated units (McLennan et al., 2013; Schmidt et al., 347 2014; Thompson et al., 2016; Yen et al., 2017; Berger et al., 2020). The link between the Sheepbed 348 member mudstone and a basaltic source is based partly on the preservation of the basaltic bulk 349 chemical composition due to nearly isochemical alteration (McLennan et al., 2013; Vaniman et 350 al., 2014). The provenance of the Murray formation and Glen Torridon is less certain because the 351 bulk chemical composition deviates from the average basaltic martian crust, having ~10% higher SiO_2 (48 ± 10 wt%), ~35% lower MgO (5.6 ± 2.2 wt%), ~40% lower CaO (4.3 ± 2.2 wt%), and 352 353 almost 4 times higher Zn. Berger et al. (2020) used geochemical models of the fractionation and/or 354 crystal sorting via magmatic evolution of rocks with a basaltic mineral assemblage containing 355 olivine, plagioclase, and clinopyroxene (Stanley & Madeisky, 1996) to reason that the Murray 356 formation bedrock has a soil-like basaltic provenance, and that open-system chemical alteration 357 resulted in the depletion of Mg, Ca, and Mn and the passive enrichment of Si in altered residue. 358 The bulk chemical composition of the Glen Torridon bedrock has the same overall chemical 359 characteristics of the Murray formation (Data Set S1) (O'Connell-Cooper et al., 2021), and we 360 extend that interpretation to include the rocks in the region. The mineral assemblage of plagioclase, 361 pyroxene, and Fe-oxides is present in the drilled sediment samples, which is also consistent with 362 a basaltic protolith and/or altered basaltic material (e.g., Rampe et al., 2020). Therefore, the 363 provenance of most of the mudstone-dominated sedimentary units in Gale crater is likely basaltic, 364 having a soil-like composition and primary MnO concentration of 0.42 ± 0.04 wt%.

365 The basaltic provenance is key for tracing the fate of Mn in the Gale crater sediment because the element occurs as Mn^{2+} via substitution with Fe^{2+} in primary olivine and pyroxene in terrestrial 366 367 basalts and basaltic martian meteorites (Figure 6) (Papike et al., 2009). Indeed, the consistency of 368 the Fe-Mn systematics of pyroxene and olivine makes Fe/Mn diagnostic of planetary basalts 369 (Papike et al., 2009). In martian meteorites, the mean Fe/Mn of pyroxene and olivine is 370 respectively 33 ± 3 and 50 ± 3 (Figure 6). The mean Fe/Mn of bulk analyses is intermediate: 40 ± 3 371 8. The regolith breccia meteorite NWA7034, which has a bulk composition more similar to the 372 APXS analyses on Mars than other meteorites, has a bulk $Fe/Mn = of 47 \pm 9$, and the pyroxenes 373 have the same Fe/Mn as other martian meteorites (Agee et al., 2013). The mean bulk MnO of basaltic martian meteorites is 0.46 ± 0.07 wt% (Papike et al., 2009), which is effectively the same

375 range of concentrations found in the basaltic soils measured by the Mars Exploration Rover (MER)

and MSL APXS instruments (O'Connell-Cooper et al., 2017; Yen et al., 2005).

In summary, the provenance of the mudstone-dominated units is consistent with a basaltic protolith, and the Fe and Mn systematics of martian basalt are well constrained. We therefore conclude that depletions and enrichments in Mn, relative to martian basalt, can be used to trace alteration of the parent materials and mobility of the element in fluids.

381 **4.1.2.** Physical sorting during sediment transport?

382 Because the bedrock units in Gale crater are sedimentary, we ask: can the apparent depletion 383 in Mn be caused during sediment transport by physical *sorting* of basaltic sediment? We can infer 384 the MnO, FeO, and Fe/Mn of the primary Mn-bearing minerals olivine and pyroxene from martian 385 meteorites (Papike et al., 2009) to test this hypothesis. We calculated the likely FeO and Fe/Mn 386 changes caused by physical sorting using the proportions of olivine, pyroxene, and X-ray 387 amorphous material measured in soil by CheMin (Blake et al., 2013), and several hypothetical 388 sorting scenarios are possible (Figure 7). (1) If hydrodynamic sorting caused the removal of the 389 primary Mn-bearing minerals pyroxene and olivine at roughly the same proportions, then the FeO 390 would decrease, and Fe/Mn would increase. (2) If the ratio Px/(Px+OI) (Px = pvroxene: OI = 391 olivine) decreased due to olivine accumulation, then FeO and Fe/Mn would increase. (3) If 392 Px/(Px+Ol) increased due to olivine removal, then FeO and Fe/Mn would decrease, reflecting the 393 lower FeO and Fe/Mn of pyroxene. (4) If Px/(Px+Ol) decreased due to pyroxene removal, then 394 FeO and Fe/Mn would increase. These hypothetical sorting trends are not observed in the Gale 395 crater bedrock; Fe/Mn is significantly higher than expected from martian meteorite data and the 396 Fe concentrations are largely within the range of soil (Figure 7). Thus, the depletion of Mn due to 397 the alteration of primary pyroxene and olivine is more plausible than physical sorting as an 398 explanation for low Mn concentrations.

399 4.1.3. Mn leaching via chemical alteration

Leaching of Mn from bedrock is exemplified by the fracture-associated haloes in Gale crater because the alteration occurred in situ and the bedrock adjacent to the haloes provides an unambiguous parent composition (Yen et al., 2017). Two haloes in the Stimson formation were

403 investigated by drilling four holes: two within ~50-cm-wide light-toned halos around fractures that 404 cross-cut strata (Greenhorn and Lubango), and two in the host bedrock adjacent to the haloes (Big 405 Sky and Okoruso). The haloes are also present in the Murray formation, and one was analyzed by 406 the APXS in a similar fashion by analyzing the light-toned material (Cody) and the adjacent host 407 bedrock (Ferdig). Relative to the host bedrock, the haloes have higher Si, Ti, S, and P and lower 408 Al, Fe, Mn, Mg, Ni, Zn, and Cr (Figures 5 and S4). Aside from the addition of Ca-sulfate (anhydrite 409 and bassanite), all of the crystalline material in the host rock decreases relative to the haloes, and 410 the X-ray amorphous fraction increases ~100-200% (Yen et al., 2017). The likely Mn-bearing 411 mineral pyroxene decreases by ~50-60%; olivine is not present in the parent or the haloes, and if 412 it was present in the parent, it may have been converted to magnetite by oxidative alteration (Yen 413 et al., 2017). The element enrichments and depletions are consistent with alteration by acidic fluids 414 that leached most of the cations, leaving a Si-, Ti-, and P-enriched residue (Yen et al., 2017). The 415 haloes therefore demonstrate that Mn leaching did occur at those locations.

416 The interpreted Mn leaching in the haloes can be extended to the mudstone-dominated 417 sedimentary units. In those units, mobilization and depletion of Mn is also reflected in the passive 418 Si enrichment and depleted Mg and Ca (Berger et al., 2020). Overall, depletion of Mn is most 419 likely tied to the alteration of Mn-bearing olivine and pyroxene. This hypothesis can be tested by 420 examining the relationship between mineralogy and chemistry. Comparing olivine + pyroxene 421 concentrations in the bedrock samples analyzed by CheMin XRD with MnO concentrations 422 (Figure 8a) and Fe/Mn (Figure 8b) shows a plausible correlation between the amount of Mn-423 bearing crystalline material and elemental Mn concentrations. The haloes, compared to their 424 basaltic parent, are depleted in Mn by \sim 70% and olivine + pyroxene by \sim 60%. Assuming the 425 provenance of the lacustrine and fluvio-lacustrine samples is soil-like basaltic material (except for 426 Windjana), depletion in olivine + pyroxene generally correlates with lower Mn. Iron is not depleted 427 in the bedrock samples, thus Fe/Mn increases.

Stability models for Mn constrain the Eh and pH conditions under which Mn²⁺ can be soluble in relevant water compositions derived from Snake River Plains Basalt aquifers (Figure 9) (Wood & Low, 1988). Contrasting Fe and Mn stability further constrains likely Eh and pH. Depletion of both Mn and Fe in the haloes indicates that both elements were soluble, which conveniently places limits on the fluid Eh-pH as oxidizing-low pH through reduced, moderate pH values (light blue in Figure 9). Depletion of Mn and retention of Fe in the mudstone suggests an Eh-pH range where 434 Mn is soluble, but Fe is not (dark blue in Figure 9). That is, upon dissolution of olivine and/or pyroxene, fractionation of Mn and Fe was possible as Mn²⁺ was removed in fluid, whereas Fe 435 436 remained as a solid oxide/oxyhydroxide/hydroxide/sulfide. This can be compared to results from 437 the Mars Phoenix lander's Wet Chemistry Laboratory (WCL) experiment, which determined an 438 Eh of ~300 mV at a pH of 7.7 ± 0.1 for the Rosy Red sample soil solution (Figure 9) (Quinn et al., 2011). Those values place that soil sample in the Eh-pH range where Mn^{2+} is an aqueous phase 439 440 and Fe³⁺ is within a solid Fe-O-H phase. Given the abundant Fe-oxide minerals detected by CheMin, it is plausible that Mn was mobilized in the Gale crater mudstone, whereas Fe was 441 442 insoluble, under similar Eh-pH conditions (dark blue in Figure 9).

443 **4.2.** Evaporative concentration of Mn

444 To approximate the fate of Mn in an evaporitic scenario relevant to Gale crater, which is a closed basin (Cabrol et al., 1999), we ran a simple thermochemical evaporation model at 100 kPa 445 446 and 25 °C utilizing Geochemist's Workbench (GWB) software (Bethke et al., 2020). In a closed 447 basin, dissolved constituents are necessarily deposited as solids when they reach saturation due to 448 water removal by evaporation and/or freezing and sublimation. To simulate the process of brine 449 formation, a dilute starting composition was adapted from analyses of basaltic aquifers in the 450 Snake River Plains Group basalts (SRPB) in Idaho and eastern Oregon, USA (Wood & Low, 1988) 451 (summarized in Tables S4 and S5). The assumptions include (1) charge is balanced by Cl⁻, (2) Eh 452 and pH are allowed to change, (3) carbonates do not form until the final step, and (4) the system 453 is closed, except for the removal of pure water as a gas $[H_2O(g)]$. Hematite and the silica 454 polymorphs quartz, cristobalite, and tridymite were suppressed because they are typically inhibited 455 in natural low-temperature systems. Carbonate precipitation was inhibited by decreasing the initial 456 HCO₃⁻ (~220 mg/L) of the SRPB water to 0.1 mg/L. Carbonate formation (including Ca-, Mg-, 457 Fe-, and Mn-carbonates) was limited in the model because they are not detected >1 wt% in Gale 458 crater rocks and soils measured with CheMin X-ray diffraction (XRD) and SAM EGA (Rampe et al., 2020; Sutter et al., 2018). The resulting HCO_3^{-1}/SO_4^{2-} (~1.5x10⁻³) is plausible for a S-rich 459 460 martian system (e.g., Penelope L. King & McLennan, 2010). The model was run in ~62,000 steps 461 to simulate the evaporation of 99.99% of the initial water [reaction: $H_2O(l) \Rightarrow H_2O(g)$], and the minerals precipitated were allowed to react with the evolving solution. Kinetic effects at high ionic 462 463 strength are not considered in the model. GWB evaporation models that simulated 99.99%

Confidential manuscript for JGR-Planets

464 evaporation of Mars-relevant solutions have been presented previously (Tosca et al., 2005), and 465 kinetic effects were also assumed to be negligible based on prior work (Harvie et al., 1984). We 466 acknowledge that the modeled pressure and temperature are not appropriate for Mars and that 467 freezing and sublimation also remove pure H_2O ; nonetheless, we model evaporation for simplicity 468 and to avoid disequilibrium effects such as brine trapped in ice.

469 The model results for the SRPB fluid are shown in Figure 10, where we present the molality 470 of aqueous Mn species ($\geq 10^{-10}$) and the saturation of Mn-bearing solids. Saturation is represented by Q/K, where Q is the ratio of component activities and K is the ratio of component activities 471 472 when the fluid is in equilibrium (e.g., Langmuir, 1997). Thus, the solution is saturated with respect 473 to a phase when O/K > 1. The evaporation model indicates that the fluid is undersaturated in Mn-474 bearing solids throughout the 99.99% evaporation, and Mn²⁺ is concentrated in Mn-species in the 475 brine: for example, Mn²⁺(aq), MnCl₂(aq), and MnCl₃-(aq) (Figure 10a). In the simulation, goethite, 476 talc, and hydroxyapatite were supersaturated under all conditions. Amorphous silica is saturated 477 with $\sim 30\%$ of the water remaining, gypsum is saturated with $\sim 3\%$ of the water remaining, and 478 dolomite, halite, and sylvite are saturated in the final step with 0.01% of the water remaining.

479 In summary, this simple evaporation model suggests that it may be possible to concentrate 480 dissolved Mn in a brine within a basaltic aquifer. Manganese remains soluble during evaporation 481 and no Mn minerals are predicted to form after 99.99% evaporation. By testing this simulation, we 482 are not implying that it is a comprehensive model for the processes that concentrated Mn in Gale 483 crater. In particular, it does not account for the substitution of Mn in other minerals common in 484 Gale crater (e.g., magnetite, hematite) (Rampe et al., 2020), nor does it include sorption, which are 485 both processes that could have affected Mn mobility. However, concentration of Mn in brine after 486 dissolution of olivine and/or pyroxene is a plausible process that fits the depleted bedrock and 487 localized enrichments observed by Curiosity.

488 **4.3. Precipitation of Mn in localized features**

The Mn-bearing phase(s) in the Mn-rich features that *Curiosity* discovered has(have) not been unambiguously identified (cf. Lanza et al., 2016). The occurrence in veins, nodules, and coatings, and co-enrichments in Cl, P, Zn, and Fe (Figure 4) are consistent with concentration and precipitation from fluids. However, the rover's instrumentation is limited and identifying Mnbearing phases is not straightforward. Nor has it been straightforward to determine if the Mn is 494 adsorbed to surfaces and/or contained within amorphous material, rather than incorporated in 495 crystalline minerals. Most Mn-rich targets have been too small and/or breakable to safely drill and 496 deliver material to CheMin and SAM for XRD and EGA measurements. The exception is the target 497 Groken (sols 2906-2921), which has mm-scale, dark nodules enriched in Mn and P, as determined 498 by a raster of the adjacent nodular target Ayton (Figure 3i, 4c, 4d). The nodule-rich bedrock at the 499 Groken/Ayton site was drilled and analyzed by CheMin and SAM, and preliminary results suggest 500 that the Mn- and P-bearing phase(s) may not be identifiable unambiguously with XRD or EGA, 501 but that EGA indicates Mn may have a 2+ oxidation state (Berger et al., 2021; J. V. Clark et al., 502 2021; Lanza et al., 2021; Thorpe et al., 2021; Treiman et al., 2021). Despite the ambiguities, we 503 can apply the principle of parsimony to constrain the Mn-rich occurrences, and below we discuss 504 Mn oxidation and possible Mn-bearing phases. We do not consider Mn adsorption to explain the 505 Mn-rich features because that process is unlikely to result in Mn concentrations of more than 1 506 wt% (e.g., Groeningen et al., 2020; Kebabi et al., 2017).

507 Manganese enrichment by oxidation of dissolved Mn^{2+} is remarkable for an aqueous system 508 in Gale crater because, at pH >2 and under Mars's atmosphere, the Mn oxidation reaction to form 509 pyrolusite,

510 $Mn^{2+} + 2H_2O \rightarrow Mn^{IV}O_2 + 4H^+ + 2e^-$ (Eqn. 1)

511 ($E^{\circ} = -1.23V$),

is non-spontaneous and has a negative electrochemical potential (E° at STP). Thus, a strong oxidant is necessary to induce precipitation of Mn as an oxide. Oxychlorine species are strong oxidants and have been identified in Gale crater bedrock (J. V. Clark et al., 2021; Ming et al., 2014; Sutter et al., 2018) and by the Wet Chemistry Laboratory on *Phoenix* (Kounaves et al., 2010, 2014). Specifically, perchlorate ($Cl^{VII}O_4^{-}$) and chlorate ($Cl^{IV}O_3^{2-}$) were detected by Sutter et al. (2018).

517 In theory, perchlorate oxidizes
$$Mn^{2+}$$
 spontaneously:

518 $ClO_4^- + Mn^{II} + 4H^+ + 6e^- \rightarrow Mn^{IV}O_2 + Cl^- + 2H_2O$ (Eqn. 2)

519 ($E^{\circ} = +0.11V$).

- 520 However, perchlorate is kinetically inhibited at low temperatures, and it may be inert as an oxidant,
- as suggested by experiments with Fe (Mitra & Catalano, 2019). Oxidation by chlorate is favored
- 522 because the reaction is spontaneous with higher E°:
- 523 $ClO_3^- + Mn^{2+} + 2H^+ + 4e^- \rightarrow Mn^{IV}O_2 + Cl^- + H_2O$ (Eqn. 3)
- 524 ($E^{\circ} = +0.185V$).

525 Chlorate is kinetically reactive at low temperatures; for example, it oxidizes Fe²⁺ in experimental 526 setups at pH 3-7 (Mitra & Catalano, 2019). However, the reaction rate for Eqn. 3 is currently 527 unknown in a natural system.

528 It is possible that Mn-rich features preserve a primary 2+ oxidation state for Mn in carbonates, 529 chlorides, and/or phosphates. In aqueous systems derived from a basaltic crust and containing 530 HCO_3^- that is buffered to 6.5 < pH < 10.5 by a basaltic mineral assemblage, carbonates reach 531 saturation and can precipitate readily (e.g., King et al., 2004). Evidence of carbonates via C 532 detections (above the atmospheric background) in the Mn-rich features has not been reported 533 (Lanza et al., 2016); however, the detection limit for carbonate may be too high (~20 wt%) to 534 identify carbonates reliably (Anderson et al., 2017). In addition, CheMin has not found carbonates 535 >1 wt% with X-ray diffraction. Mn-chlorides may be possible because two targets are highly enriched in Mn and Cl at a molar ratio (Mn/Cl ~ 0.62) that is similar to MnCl₂ (Mn/Cl = 0.5) (Figure 536 537 4a, 4b). Possible phases are anhydrous Mn-chloride (Mn^{II}Cl₂) or tetrahydrate Mn chloride 538 $(Mn^{II}Cl_2(H_2O)_4)$. Phosphates are another possibility, including Mn-sarcopside $(Mn^{II}_3(PO_4)_2)$ or 539 $Mn^{II}HPO_4$. However, the ratio of MnO to P_2O_5 observed in the targets with the highest 540 concentrations of the two oxides does not match the stoichiometry of those Mn-phosphate phases 541 (Figure 4d). A jahnsite-whiteite group mineral has been proposed for the Mn-and P-rich targets, 542 but this interpretation is speculative (Berger et al., 2021; Treiman et al., 2021). Overall, the 543 presence of Fe³⁺ oxides in CheMin samples (Rampe et al., 2020) indicates that late-stage diagenetic 544 fluids in Gale crater were above the hematite-magnetite buffer, and the relevant anionic species do 545 not tend to change appreciably at conditions between hematite-magnetite, unless pH changes. 546 Chlorides and phosphates are possible, but unlikely relative to the solids with other major cations 547 (Fe, Mg, Ca).

548 We find that there is not one single phase or assemblage of phases that characterizes the Mn 549 enrichments, and that this is consistent with the formation of the features from the evaporation, sublimation, and/or freezing of a brine with concentrated conservative elements including Mn, Fe, P, Cl, and/or Zn. If a brine or sedimentary system undergoes episodic flooding (water addition) and then re-evaporation even once (let alone tens to millions of times), then more complexity may arise. Indeed, K-Ar dating of jarosite at 2.12 ± 0.36 Ga in a Gale crater mudstone is evidence of post-depositional fluid flow and salt formation as recent as the Amazonian (Martin et al., 2017). The variability of the enrichments over the traverse, even within bedrock having a relatively uniform composition, is also consistent with this interpretation.

557 **5.** Conclusions

558 Our interpretation of the occurrence of Mn in Gale crater, as measured by the APXS, is that 559 Mn was mobile in fluids, as evident in depleted bedrock, depleted alteration haloes, and highly enriched veins, nodules, and coatings. Mn²⁺ was likely released into fluids via alteration of a 560 basaltic precursor, and then subsequently concentrated in brine(s) that resulted from evaporation, 561 sublimation, and/or freezing of Gale crater fluids, such that Mn²⁺ would be enriched when the 562 liquid water was removed. Dissolved Mn species would necessarily precipitate when >99% of the 563 564 water was removed. This scenario is consistent with the highly localized, Mn-rich veins, nodules, 565 and coatings in Gale crater, which contain widely variable associations of Mn with high 566 concentrations of Fe, Cl. P, and/or Zn. Variability in the Mn-rich features suggests that complex 567 mixtures of phases precipitated from brine(s). It is plausible that the localized enrichments preserve 568 mass balance for Mn in the closed basin of Gale crater because the extensive leaching of Mn from 569 thick sedimentary units may be accounted for in the high-Mn features. Manganese is utilized in 570 reduction-oxidation biochemical reactions as an energy source for life, and thus evidence of Mn 571 mobility in fluids has important implications for habitability in Gale crater.

572 Acknowledgements

573 This research was funded by the Canadian Space Agency, NASA-JPL-Caltech, NASA-JSC, 574 USRA NPP, and the Australian Research Council grant DP200100406. The APXS data are 575 archived at the Planetary Data System (MSL APXS RDR dataset: 10.17189/1518757).

576 Figures

577 Figure 1: 578 *Curiosity*'s 579 traverse and 580 locations of APXS 581 targets up to sol 582 3076. The Murray 583 formation and Glen 584 Torridon region make up the Mount 585 586 Sharp group. The 587 rover's traverse is 588 the white line from 589 Bradbury Landing 590 on sol 0 up to the 591 Nontron drill site 592 on sol 3076 and the 593 symbols APXS 594 correspond with 595 figures in the 596 manuscript. 597 Selected waypoints and outcrop on the 598 599 traverse are 600 indicated. The 601 geologic units and 602 topographic 603 contour lines are 604 adapted from 605 (Grotzinger et al., 606 2015). 607



Figure 2: Plots of (a) Mn, 608 609 (b) Cl, (c) P₂O₅, (d) Zn, and 610 (e) molar Fe/Mn versus sol 611 (sols 0-3076), covering 612 APXS results over the entire MSL mission from 613 614 landing up to the Nontron 615 drill site in the Glen 616 Torridon region. Average 617 Gale crater soil $\pm 2\sigma$ is 618 denoted (horizontal brown 619 lines). Selected Mn-rich 620 indicated: targets are 621 Stephen (St), Garden City 622 Newport (GC), Ledge 623 (NL), Timber Point (TPt), 624 Jones Marsh (JM), 625 Abernethy (Ab), 626 Dunbartonshire (D), and 627 Ayton (Ay). See Section 2 628 for explanation of the data. 629





Figure 3: Images of representative Mn-rich targets Stephen, Newport Ledge, Jones Marsh, 630 631 Dunbartonshire, Ayton, and Trow. Yellow circles in MAHLI images denote the approximate 632 APXS FOV. (a) Mastcam context mosaic of the Windjana drill site (WJ) before drilling, including the Zn-rich target Stephen (MnO = 4.05 ± 0.06 wt%). (b) MAHLI image of Stephen after the dust 633 634 was removed by ChemCam (the APXS measurement was after dust removal). The adjacent Mnrich ChemCam target Neil is indicated. The APXS FOV indicates the center of the 5-point APXS 635 raster of the target. (c) Navcam context mosaic of Newport Ledge (MnO = 2.27 ± 0.05 wt%). 636 637 Mastcam images (inset) show the post-APXS ChemCam analysis of Newport Ledge, which 638 removed dust and exposed the dark surface. (d) MAHLI image of Newport Ledge, which has a 639 relatively continuous coating of dark material. (e) Navcam context mosaic of the P-rich Jones 640 Marsh target (MnO = 3.99 ± 0.09 wt%), a patchy coating of dark material. (f) MAHLI image of

641 Jones Marsh shows the contrast of the patchy dark coating with the lighter-toned bedrock. (g) Confidential manuscript for JGR-Planets

- 642 Mastcam mosaic of the Hutton drill site before drilling, showing Dunbartonshire (MnO = $6.33 \pm$
- 643 0.13 wt%) and similar fracture-fill material (white arrows). Dunbartonshire has the highest MnO
- 644 discovered in Gale crater. (h) MAHLI image of fracture-associated Dunbartonshire. (i) MAHLI
- 645 image of the Ayton and Trow rasters (MnO up to 2.44 ± 0.05 wt%), which is ~15 cm adjacent to 646 the Groken drill site and is associated with high P₂O₅ (up to 5.49 ± 0.28 wt%). Images details are
- 647 provided in Table S2.
- 648

649 Figure 4: Plots of MnO concentrations 650 versus (a, b) Cl, (c, d) P_2O_5 , (e, f) Zn, and (g, h) FeO. The data and notations 651 652 are the same as described in Figure 2. The left column (a, c, e, g) plots data on 653 654 a log scale; the right column (b, d, f, h) 655 plots the same data on a linear scale for 656 comparison. Simple addition models for 657 MnO_2 , $Mn_3(PO_4)_2$, $MnH(PO_4)$, and 658 MnCl₂ are shown as vectors in (a-d). 659 The depletion trends of Mn, Zn, and 660 FeO in the Buckskin-type silica-rich 661 facies and silica-rich fracture haloes is 662 indicated by arrows in (e) and (g). The mugearitic Bradbury group targets have 663 664 lower MnO and FeO that is attributed to 665 processes, and they igneous are 666 enclosed by a polygon in (g). 667





669 Figure 5: MnO and FeO concentrations in the mudstone-dominated units (a, b) compared to the 670 sandstone of the Stimson formation (c, d). MnO and Fe/Mn versus FeO in (a) and (b) demonstrate 671 that the lesser MnO relative to the basaltic soil does not have a corresponding change in FeO. Two 672 exceptions (arrows) are: (1) the Buckskin high-silica facies, which is a thin (< 5 m thickness) layer 673 in the Pahrump Hills member of the Murray formation and (2) a silica-rich halo (Cody and Ferdig 674 sol 1109). In contrast, MnO depletion in the Stimson formation (c, d) has a corresponding decrease in FeO and a lower magnitude of Fe/Mn increase. The MnO depletion in the Stimson is limited to 675 676 fracture associated haloes (arrows) (Yen et al., 2017). Error bars are omitted for clarity in (b); 677 typical error for Fe/Mn values above 100 is ~5-10% for overnight integrations and ~15-35% for 678 short integrations and larger standoff measurements. Error for Fe/Mn < 100 is typically smaller 679 than the symbols (3-5%). Ten targets with MnO above 0.9 wt% are not shown in (a) and (b).

Confidential manuscript for JGR-Planets



681 682

Figure 6: MnO and FeO concentrations in martian meteorites compared to APXS measurements of Gale crater soils on a S- and Cl-free basis. (a) MnO versus FeO and (b) Fe/Mn versus FeO are shown for bulk meteorites and average microprobe analyses of pyroxenes and olivines (Papike et al., 2009). Each pyroxene and olivine point represents ~50 individual analyses of the mineral in one meteorite. The 12 Gale crater soil compositions are enclosed in the red polygon. The Fe/Mn of each group is shown in (b).



691 Figure 7: Modeled Fe/Mn and FeO changes under hypothetical conditions that can change Mn 692 concentrations and are relevant to Gale crater. The physical sorting of the principal Mn-bearing 693 phases derived from a soil-like basaltic protolith (pyroxene and olivine) can control changes in 694 FeO content and small changes in Fe/Mn. This would occur if the bulk proportions of the minerals 695 were changed by physical transport processes capable of sorting Mn-bearing phases based on, for 696 example, differences in density or grain size (e.g., Thorpe et al., 2019). Such processes could result 697 in the accumulation (enrichment) or removal (depletion) of Mn-bearing minerals. Addition of Fe as a cement could also result in detectable changes in FeO and Fe/Mn. In contrast, the removal of 698 699 Mn in solution via olivine and pyroxene dissolution in a system where Fe-oxides are insoluble 700 would result in an increase in Fe/Mn with minimal or zero change in FeO concentrations. We 701 propose that the Mn dissolution model most plausibly fits the observed Fe/Mn and FeO in the 702 mudstone-dominated sedimentary units in Gale crater (Figure 5). Data from Figure 5b are shown 703 for comparison. 704



706 Figure 8: (a) MnO and (b) Fe/Mn versus the sum of olivine and pyroxene in CheMin samples. MnO and the Mn-bearing minerals have a positive linear correlation ($R^2 = 0.64$). Generally, a 707 decrease in olivine and pyroxene corresponds with an increase in Fe/Mn, but the apparent negative 708 709 correlation is less certain due to several outliers. The interpreted sedimentary environment of the 710 CheMin samples is denoted (Rampe et al., 2020), and lacustrine samples were in mudstone-711 dominated units. Mineral abundances are in wt% normalized to 100% without amorphous material. Two samples with high Fe/Mn (~250) are not shown in (b): Marimba and Rock Hall have 2 wt% 712 713 and 17 wt% olivine + pyroxene, respectively. CheMin data are from (Achilles et al., 2020; Bish et al., 2013; Blake et al., 2013; Rampe et al., 2017; Treiman et al., 2016; Vaniman et al., 2014; Yen 714 715 et al., 2017). 716



718 Figure 9: Superimposed Pourbaix diagrams for Mn and Fe with a water composition adapted from 719 analyses of Snake River Plains Basalt aquifers (see Tables S4 and S5 for modeling details). Fields 720 where Mn is stable as solid and aqueous phases are tan and blue, respectively, and the phase is shown in black text. Fe stability fields are denoted by red dashed lines, and Fe phases are shown 721 722 in red italics. The darker blue field indicates Eh/pH values where Mn is stable as an aqueous phase, 723 whereas Fe is stable as a solid phase; that is, Mn and Fe have the potential to fractionate into 724 respective aqueous and solid phases under these conditions. The Mars Phoenix WCL results for 725 the soil sample Rosy Red is plotted (Eh ~0.3 V; pH ~7.7) (Quinn et al., 2011).



728 Figure 10: (a) Manganese-bearing species concentrations and (b) mineral saturation (Q/K) versus 729 the percent of water remaining during modeled evaporation. The reaction $H_2O(l) \Rightarrow H_2O(g)$ run 730 iteratively simulates evaporation of 99.99% of the liquid water, which proceeds from left to right 731 on the x-axis. The initial solution is adapted from analyses of aquifers in the Snake River Plains 732 Basalt in Idaho, USA (details given in Tables S4 and S5). Concentrations of aqueous Mn species 733 above 10⁻¹⁰ molal and total dissolved Mn are shown in (a). The saturation curves of Mn-bearing 734 phases and phases that reach saturation during brine evolution (amorphous silica, gypsum, dolomite, halite, and sylvite) are shown in (b), where Q/K = 1 indicates saturation and Q/K < 1735 736 indicates undersaturation. The model indicates that no Mn-bearing phases are saturated after 737 99.99% evaporation; all of the Mn remains in solution after 99.99% evaporation. Goethite is 738 saturated under all modeled conditions. The solution pH is shown (solid black line; right axis). 739 Secondary minerals are allowed to back-react with the solution.

741 References

- Achilles, C. N., Rampe, E. B., Downs, R. T., Bristow, T. F., Ming, D. W., Morris, R. V., et al.
 (2020). Evidence for Multiple Diagenetic Episodes in Ancient Fluvial-Lacustrine
 Sedimentary Rocks in Gale Crater, Mars. *Journal of Geophysical Research: Planets*, *125*(8), e2019JE006295. https://doi.org/10.1029/2019JE006295
- Agee, C. B., Wilson, N. V., McCubbin, F. M., Ziegler, K., Polyak, V. J., Sharp, Z. D., et al.
 (2013). Unique Meteorite from Early Amazonian Mars: Water-Rich Basaltic Breccia Northwest Africa 7034. *Science*. https://doi.org/10.1126/science.1228858
- Anderson, D. E., Ehlmann, B. L., Forni, O., Clegg, S. M., Cousin, A., Thomas, N. H., et al.
 (2017). Characterization of LIBS emission lines for the identification of chlorides,
 carbonates, and sulfates in salt/basalt mixtures for the application to MSL ChemCam
 data. *Journal of Geophysical Research: Planets*, *122*(4), 744–770.
 https://doi.org/10.1002/2016JE005164
- Arvidson, R. E., Squyres, S. W., Morris, R. V., Knoll, A. H., Gellert, R., Clark, B. C., et al.
 (2016). High concentrations of manganese and sulfur in deposits on Murray Ridge,
 Endeavour Crater, Mars. *American Mineralogist*, *101*(6), 1389–1405.
 https://doi.org/10.2138/am-2016-5599
- Banham, S. G., Gupta, S., Rubin, D. M., Watkins, J. A., Sumner, D. Y., Edgett, K. S., et al.
 (2018). Ancient Martian aeolian processes and palaeomorphology reconstructed from the
 Stimson formation on the lower slope of Aeolis Mons, Gale crater, Mars. *Sedimentology*,
 65(4), 993–1042. https://doi.org/10.1111/sed.12469
- Banham, S. G., Gupta, S., Rubin, D. M., Edgett, K. S., Barnes, R., Van Beek, J., et al. (2021). A
 Rock Record of Complex Aeolian Bedforms in a Hesperian Desert Landscape: The
 Stimson Formation as Exposed in the Murray Buttes, Gale Crater, Mars. *Journal of Geophysical Research: Planets*, *126*(4), e2020JE006554.
 https://doi.org/10.1029/2020JE006554
- Berger, J. A., Schmidt, M. E., Gellert, R., Boyd, N. I., Desouza, E. D., Flemming, R. L., et al.
 (2017). Zinc and germanium in the sedimentary rocks of Gale Crater on Mars indicate
 hydrothermal enrichment followed by diagenetic fractionation. *Journal of Geophysical Research: Planets*, *122*(8), 1747–1772. https://doi.org/10.1002/2017JE005290
- Berger, J. A., Gellert, R., Boyd, N. I., King, P. L., McCraig, M. A., O'Connell-Cooper, C. D., et
 al. (2020). Elemental Composition and Chemical Evolution of Geologic Materials in
 Gale Crater, Mars: APXS Results from Bradbury Landing to the Vera Rubin Ridge. *Journal of Geophysical Research: Planets*, *125*(12), e2020JE006536.
 https://doi.org/10.1029/2020JE006536
- Berger, J. A., VanBommel, S. J. V., Clark, B. C., Gellert, R., House, C. H., King, P. L., et al.
 (2021). Manganese- and Phosphorus-Rich Nodules in Gale Crater, Mars: APXS Results
 from the Groken Drill Site. In *52nd Lunar and Planetary Science Conference* (Vol. 52, p.
 2194). Retrieved from https://ui.adsabs.harvard.edu/abs/2021LPI....52.2194B/abstract

Bethke, C. M., Farrell, B., & Sharifi, M. (2020). *The Geochemist's Workbench Release 14: GWB Essentials Guide*. Champaign, Illinois: Aqueous Solutions, LLC.

782	Bish, D. L., Blake, D. F., Vaniman, D. T., Chipera, S. J., Morris, R. V., Ming, D. W., et al.
783 784 785	(2013). X-ray Diffraction Results from Mars Science Laboratory: Mineralogy of Rocknest at Gale Crater. <i>Science</i> , <i>341</i> (6153), 1238932. https://doi.org/10.1126/science.1238932
786 787 788	 Blake, D. F., Morris, R. V., Kocurek, G., Morrison, S. M., Downs, R. T., Bish, D., et al. (2013). Curiosity at Gale Crater, Mars: Characterization and Analysis of the Rocknest Sand Shadow. <i>Science</i>, <i>341</i>(6153), 1239505. https://doi.org/10.1126/science.1239505
789 790 791	 Cabrol, N. A., Grin, E. A., Newsom, H. E., Landheim, R., & McKay, C. P. (1999). Hydrogeologic Evolution of Gale Crater and Its Relevance to the Exobiological Exploration of Mars. <i>Icarus</i>, 139(2), 235–245. https://doi.org/10.1006/icar.1999.6099
792 793 794 795	Campbell, J. L., Perrett, G. M., Gellert, R., Andrushenko, S. M., Boyd, N. I., Maxwell, J. A., et al. (2012). Calibration of the Mars Science Laboratory Alpha Particle X-ray Spectrometer. <i>Space Science Reviews</i> , 170(1–4), 319–340. https://doi.org/10.1007/s11214-012-9873-5
796 797 798	Clark, B. C., Baird, A. K., Weldon, R. J., Tsusaki, D. M., Schnabel, L., & Candelaria, M. P. (1982). Chemical composition of Martian fines. <i>Journal of Geophysical Research: Solid</i> <i>Earth</i> , 87(B12), 10059–10067. https://doi.org/10.1029/JB087iB12p10059
799 800 801 802	Clark, J., Sutter, B., Archer, P. D., Ming, D., Rampe, E., McAdam, A., et al. (2021). A Review of Sample Analysis at Mars-Evolved Gas Analysis Laboratory Analog Work Supporting the Presence of Perchlorates and Chlorates in Gale Crater, Mars. <i>Minerals</i> , <i>11</i> (5), 475. https://doi.org/10.3390/min11050475
803 804 805 806 807	Clark, J. V., Lanza, N., Rampe, E. B., Archer, P. D., Morris, R. V., Tu, V., et al. (2021). Evolved Gas Analysis of Manganese-Bearing Phases and Implications for the Sample Analysis at Mars (SAM) Instrument on Board the Curiosity Rover in Gale Crater, Mars. In 52nd Lunar and Planetary Science Conference (p. 1206). Retrieved from https://ui.adsabs.harvard.edu/abs/2021LPI52.1206C
808 809 810 811 812	 Edgar, L. A., Fedo, C. M., Gupta, S., Banham, S. G., Fraeman, A. A., Grotzinger, J. P., et al. (2020). A Lacustrine Paleoenvironment Recorded at Vera RubinRidge, Gale Crater: Overview of the Sedimentology and Stratigraphy Observed by the Mars ScienceLaboratory Curiosity Rover. <i>Journal of Geophysical Research: Planets</i>, <i>125</i>(3), e2019JE006307. https://doi.org/10.1029/2019JE006307
813 814 815	Fedo, C. M., Grotzinger, J. P., Gupta, S., Fraeman, A., Edgar, L. A., Edgett, K., et al. (2018). Sedimentology and stratigraphy of the Murray formation, Gale crater, Mars. In 49 th Lunar and Planetary Science Conference, Abstract (Vol. 2078).
816 817 818	Foley, C. N., Economou, T., & Clayton, R. N. (2003). Final chemical results from the Mars Pathfinder alpha proton X-ray spectrometer. <i>Journal of Geophysical Research: Planets</i> , 108(E12), 8096. https://doi.org/10.1029/2002JE002019
819 820 821	Forni, O., Gaft, M., Toplis, M. J., Clegg, S. M., Maurice, S., Wiens, R. C., et al. (2015). First detection of fluorine on Mars: Implications for Gale Crater's geochemistry. <i>Geophysical</i> <i>Research Letters</i> , 42(4), 2014GL062742. https://doi.org/10.1002/2014GL062742
822 823	Gabriel, T. S. J., Hardgrove, C., Achilles, C., Rampe, E. B., Czarnecki, S., Rapin, W., et al. (2019). Pervasive water-rich, fracture-associated alteration halos in Gale crater, Mars. In

- *AGU Fall Meeting Abstracts* (Vol. 43). Retrieved from
 http://adsabs.harvard.edu/abs/2019AGUFM.P43B..08G
- Gasda, P. J., Lanza, N. L., Lamm, S. N., L'Haridon, J., Meslin, P.-Y., Forni, O., et al. (2018).
 Evidence of Redox Sensitive Elements Associated with Possible Shoreline Deposits in
 Gale Crater. *Lunar and Planetary Science Conference*, (2083), 2483.
- Gellert, R., & Clark, B. C. (2015). In situ compositional measurements of rocks and soils on
 NASA's Mars rovers with the alpha-particle X-ray spectrometer (APXS). *Elements*, *11*,
 39–44.
- Gellert, R., Rieder, R., Brückner, J., Clark, B. C., Dreibus, G., Klingelhöfer, G., et al. (2006).
 Alpha Particle X-Ray Spectrometer (APXS): Results from Gusev crater and calibration
 report. *Journal of Geophysical Research*, *111*(E02S05).
 https://doi.org/200610.1029/2005JE002555
- Gellert, R., Campbell, J. L., King, P. L., Leshin, L. A., Lugmair, G. W., Spray, J. G., et al.
 (2009). The Alpha-Particle-X-Ray-Spectrometer (APXS) for the Mars Science
 Laboratory (MSL) Rover Mission. In *Lunar Planet. Sci., XL* (p. Abstract 2364).
- Groeningen, N. V., Glück, B., Christl, I., & Kretzschmar, R. (2020). Surface precipitation of Mn
 2+ on clay minerals enhances Cd 2+ sorption under anoxic conditions. *Environmental Science: Processes & Impacts*, 22(8), 1654–1665. https://doi.org/10.1039/D0EM00155D
- Grotzinger, J. P., Sumner, D. Y., Kah, L. C., Stack, K., Gupta, S., Edgar, L., et al. (2014). A
 Habitable Fluvio-Lacustrine Environment at Yellowknife Bay, Gale Crater, Mars. *Science*, 343(6169), 1242777. https://doi.org/10.1126/science.1242777
- Grotzinger, J. P., Gupta, S., Malin, M. C., Rubin, D. M., Schieber, J., Siebach, K., et al. (2015).
 Deposition, exhumation, and paleoclimate of an ancient lake deposit, Gale crater, Mars. *Science*, *350*(6257), aac7575. https://doi.org/10.1126/science.aac7575
- Harvie, C. E., Møller, N., & Weare, J. H. (1984). The prediction of mineral solubilities in natural
 waters: The Na-K-Mg-Ca-H-Cl-SO4-OH-HCO3-CO3-CO2-H2O system to high ionic
 strengths at 25°C. *Geochimica et Cosmochimica Acta*, 48(4), 723–751.
 https://doi.org/10.1016/0016-7037(84)90098-X
- Hurowitz, J. A., Grotzinger, J. P., Fischer, W. W., McLennan, S. M., Milliken, R. E., Stein, N., et
 al. (2017). Redox stratification of an ancient lake in Gale crater, Mars. *Science*, *356*(6341), eaah6849. https://doi.org/10.1126/science.aah6849
- Kebabi, B., Terchi, S., Bougherara, H., Reinert, L., & Duclaux, L. (2017). Removal of
 manganese (II) by edge site adsorption on raw and milled vermiculites. *Applied Clay Science*, 139, 92–98. https://doi.org/10.1016/j.clay.2016.12.041
- King, Penelope L., & McLennan, S. M. (2010). Sulfur on Mars. *ELEMENTS*, 6(2), 107–112.
 https://doi.org/10.2113/gselements.6.2.107
- King, P.L., Lescinsky, D. T., & Nesbitt, H. W. (2004). The composition and evolution of
 primordial solutions on Mars, with application to other planetary bodies. *Geochimica et Cosmochimica Acta*, 68, 4993–5008. https://doi.org/doi: DOI: 10.1016/j.gca.2004.05.036
- Kounaves, S. P., Hecht, M. H., Kapit, J., Gospodinova, K., DeFlores, L., Quinn, R. C., et al.
 (2010). Wet Chemistry experiments on the 2007 Phoenix Mars Scout Lander mission:

- Bata analysis and results. *Journal of Geophysical Research*, *115*, 16 PP.
 https://doi.org/201010.1029/2009JE003424
- Kounaves, S. P., Chaniotakis, N. A., Chevrier, V. F., Carrier, B. L., Folds, K. E., Hansen, V. M.,
 et al. (2014). Identification of the perchlorate parent salts at the Phoenix Mars landing site
 and possible implications. *Icarus*, 232, 226–231.
 https://doi.org/10.1016/j.icarus.2014.01.016
- 871 Langmuir, D. (1997). Aqueous Environmental Geochemistry. Prentice Hall.
- Lanza, N. L., Fischer, W. W., Wiens, R. C., Grotzinger, J., Ollila, A. M., Cousin, A., et al.
 (2014). High manganese concentrations in rocks at Gale crater, Mars. *Geophysical Research Letters*, 41(16), 5755–5763. https://doi.org/10.1002/2014GL060329
- Lanza, N. L., Wiens, R. C., Arvidson, R. E., Clark, B. C., Fischer, W. W., Gellert, R., et al.
 (2016). Oxidation of manganese in an ancient aquifer, Kimberley formation, Gale crater,
 Mars. *Geophysical Research Letters*, 43(14), 7398–7407.
 https://doi.org/10.1002/2016GL069109
- Lanza, N. L., Gasda, P., Ari, E., Comellas, J., Caravaca, G., Rampe, E. B., et al. (2021).
 CHEMISTRY OF MANGANESE-BEARING MATERIALS AT THE GROKEN DRILL
 SITE, GALE CRATER, MARS. In *52nd Lunar and Planetary Science Conference*. The
 Woodlands, United States: Lunar and Planetary Institute. Retrieved from
 https://hal.archives-ouvertes.fr/hal-03143136
- Lasue, J., Clegg, S. M., Forni, O., Cousin, A., Wiens, R. C., Lanza, N., et al. (2016). Observation
 of > 5 wt % zinc at the Kimberley outcrop, Gale crater, Mars. *Journal of Geophysical Research: Planets*, *121*(3), 338–352. https://doi.org/10.1002/2015JE004946
- L'Haridon, J., Mangold, N., Fraeman, A. A., Johnson, J. R., Cousin, A., Rapin, W., et al. (2020).
 Iron Mobility during Diagenesis at Vera Rubin ridge, Gale Crater, Mars. *Journal of Geophysical Research: Planets*, n/a(n/a), e2019JE006299.
 https://doi.org/10.1029/2019JE006299
- Martin, P. E., Farley, K. A., Baker, M. B., Malespin, C. A., Schwenzer, S. P., Cohen, B. A., et al.
 (2017). A Two-Step K-Ar Experiment on Mars: Dating the Diagenetic Formation of
 Jarosite from Amazonian Groundwaters. *Journal of Geophysical Research: Planets*, *122*(12), 2803–2818. https://doi.org/10.1002/2017JE005445
- McLennan, S. M., Anderson, R. B., Bell, J. F., Bridges, J. C., Calef, F., Campbell, J. L., et al.
 (2013). Elemental Geochemistry of Sedimentary Rocks at Yellowknife Bay, Gale Crater,
 Mars. Science, 1244734. https://doi.org/10.1126/science.1244734
- Milliken, R. E., Grotzinger, J. P., & Thomson, B. J. (2010). Paleoclimate of Mars as captured by
 the stratigraphic record in Gale Crater. *Geophysical Research Letters*, 37, 6 PP.
 https://doi.org/201010.1029/2009GL041870
- Ming, D. W., Gellert, R., Morris, R. V., Arvidson, R. E., Brückner, J., Clark, B. C., et al. (2008).
 Geochemical properties of rocks and soils in Gusev Crater, Mars: Results of the Alpha
 Particle X-Ray Spectrometer from Cumberland Ridge to Home Plate. *Journal of Geophysical Research*, *113*(E12S39), 28 PP. https://doi.org/200810.1029/2008JE003195

- Ming, D. W., Archer, P. D., Glavin, D. P., Eigenbrode, J. L., Franz, H. B., Sutter, B., et al.
 (2014). Volatile and Organic Compositions of Sedimentary Rocks in Yellowknife Bay,
 Gale Crater, Mars. *Science*, *343*(6169), 1245267.
 https://doi.org/10.1126/science.1245267
- Mitra, K., & Catalano, J. G. (2019). Chlorate as a Potential Oxidant on Mars: Rates and Products
 of Dissolved Fe(II) Oxidation. *Journal of Geophysical Research: Planets*, *124*(11),
 2893–2916. https://doi.org/10.1029/2019JE006133
- Morris, R. V., Vaniman, D. T., Blake, D. F., Gellert, R., Chipera, S. J., Rampe, E. B., et al.
 (2016). Silicic volcanism on Mars evidenced by tridymite in high-SiO2 sedimentary rock at Gale crater. *Proceedings of the National Academy of Sciences*, *113*(26), 7071–7076.
 https://doi.org/10.1073/pnas.1607098113
- Morrison, S. M., Downs, R. T., Blake, D. F., Vaniman, D. T., Ming, D. W., Hazen, R. M., et al.
 (2018). Crystal chemistry of martian minerals from Bradbury Landing through Naukluft
 Plateau, Gale crater, Mars. *American Mineralogist*, *103*(6), 857–871.
 https://doi.org/10.2138/am.2018.6124
- 919 https://doi.org/10.2138/am-2018-6124
- Nachon, M., Clegg, S. M., Mangold, N., Schröder, S., Kah, L. C., Dromart, G., et al. (2014).
 Calcium sulfate veins characterized by ChemCam/Curiosity at Gale crater, Mars. *Journal* of Geophysical Research: Planets, 119(9), 1991–2016.
 https://doi.org/10.1002/2013JE004588
- Nachon, M., Mangold, N., Forni, O., Kah, L. C., Cousin, A., Wiens, R. C., et al. (2017).
 Chemistry of diagenetic features analyzed by ChemCam at Pahrump Hills, Gale crater, Mars. *Icarus*, 281, 121–136. https://doi.org/10.1016/j.icarus.2016.08.026
- O'Connell-Cooper, C. D., Spray, J. G., Thompson, L. M., Gellert, R., Berger, J. A., Boyd, N. I.,
 et al. (2017). APXS-derived chemistry of the Bagnold dune sands: Comparisons with
 Gale Crater soils and the global Martian average. *Journal of Geophysical Research: Planets*, *122*(12), 2623–2643. https://doi.org/10.1002/2017JE005268
- O'Connell-Cooper, C. D., Thompson, L. M., Gellert, R., Spray, J. G., Boyd, N. I., Berger, J., et
 al. (2021). APXS Geochemistry of the Fractured Intermediate Unit (fIU) Its
 Relationship to Underlying Glen Torridon Units and Overlying Pediment Rocks at the
 Greenheugh Unconformity. In *52nd Lunar and Planetary Science Conference* (p. 2405).
 Retrieved from https://ui.adsabs.harvard.edu/abs/2021LPI....52.2405O
- Papike, J. J., Karner, J. M., Shearer, C. K., & Burger, P. V. (2009). Silicate mineralogy of
 martian meteorites. *Geochimica et Cosmochimica Acta*, 73(24), 7443–7485.
 https://doi.org/10.1016/j.gca.2009.09.008
- Quinn, R. C., Chittenden, J. D., Kounaves, S. P., & Hecht, M. H. (2011). The oxidationreduction potential of aqueous soil solutions at the Mars Phoenix landing site. *Geophysical Research Letters*, 38(14). https://doi.org/10.1029/2011GL047671
- Rampe, E. B., Ming, D. W., Blake, D. F., Bristow, T. F., Chipera, S. J., Grotzinger, J. P., et al.
 (2017). Mineralogy of an ancient lacustrine mudstone succession from the Murray
 formation, Gale crater, Mars. *Earth and Planetary Science Letters*, 471, 172–185.
 https://doi.org/10.1016/j.epsl.2017.04.021

- Rampe, E. B., Blake, D. F., Bristow, T. F., Ming, D. W., Vaniman, D. T., Morris, R. V., et al.
 (2020). Mineralogy and geochemistry of sedimentary rocks and eolian sediments in Gale
 crater, Mars: A review after six Earth years of exploration with Curiosity. *Geochemistry*,
 125605. https://doi.org/10.1016/j.chemer.2020.125605
- Rice, M. S., Gupta, S., Treiman, A. H., Stack, K. M., Calef, F., Edgar, L. A., et al. (2017).
 Geologic overview of the Mars Science Laboratory rover mission at the Kimberley, Gale
 crater, Mars. *Journal of Geophysical Research: Planets*, *122*(1), 2016JE005200.
 https://doi.org/10.1002/2016JE005200
- Schmidt, M. E., Campbell, J. L., Gellert, R., Perrett, G. M., Treiman, A. H., Blaney, D. L., et al.
 (2014). Geochemical diversity in first rocks examined by the Curiosity Rover in Gale
 Crater: Evidence for and significance of an alkali and volatile-rich igneous source. *Journal of Geophysical Research: Planets*, 119(1), 64–81.
 https://doi.org/10.1002/2013JE004481
- Schmidt, M. E., Perrett, G. M., Bray, S. L., Bradley, N. J., Lee, R. E., Berger, J. A., et al. (2018).
 Dusty Rocks in Gale Crater: Assessing Areal Coverage and Separating Dust and Rock
 Contributions in APXS Analyses. *Journal of Geophysical Research: Planets*, *123*(7),
 1649–1673. https://doi.org/10.1029/2018JE005553
- Stack, K. M., Grotzinger, J. P., Lamb, M. P., Gupta, S., Rubin, D. M., Kah, L. C., et al. (2019).
 Evidence for plunging river plume deposits in the Pahrump Hills member of the Murray
 formation, Gale crater, Mars. *Sedimentology*, *66*(5), 1768–1802.
 https://doi.org/10.1111/sed.12558
- Stanley, C. R., & Madeisky, H. E. (1996). Lithogeochemical exploration for metasomatic zones
 associated with hydrothermal mineral deposits using Pearce element ratio analysis:
 Mineral Deposit Research Unit. University of British Columbia, Short Course Notes.
- Stein, N. T., Quinn, D. P., Grotzinger, J. P., Fedo, C., Ehlmann, B. L., Stack, K. M., et al. (2020).
 Regional Structural Orientation of the Mount Sharp Group Revealed by In Situ Dip
 Measurements and Stratigraphic Correlations on the Vera Rubin Ridge. *Journal of Geophysical Research: Planets*, *125*(5), e2019JE006298.
 https://doi.org/10.1029/2019JE006298
- Sutter, B., McAdam, A. C., Mahaffy, P. R., Ming, D. W., Edgett, K. S., Rampe, E. B., et al.
 (2018). Evolved gas analyses of sedimentary rocks and eolian sediment in Gale Crater,
 Mars: Results of the Curiosity rover's sample analysis at Mars instrument from
 Yellowknife Bay to the Namib Dune. *Journal of Geophysical Research: Planets*, *122*(12), 2574–2609. https://doi.org/10.1002/2016JE005225
- Taylor, S. R., & McLennan, S. (2010). *Planetary Crusts: Their Composition, Origin and Evolution* (1st ed.). Cambridge University Press.
- Thompson, L. M., Schmidt, M. E., Spray, J. G., Berger, J. A., Fairén, A. G., Campbell, J. L., et
 al. (2016). Potassium-rich sandstones within the Gale impact crater, Mars: The APXS
 perspective. *Journal of Geophysical Research: Planets*, *121*(10), 1981–2003.
 https://doi.org/10.1002/2016JE005055
- Thompson, L. M., Berger, J. A., Spray, J. G., Fraeman, A. A., McCraig, M. A., O'Connell Cooper, C. D., et al. (2020). APXS-Derived Compositional Characteristics of Vera Rubin

988 989 990	Ridge and Murray Formation, Gale Crater, Mars: Geochemical Implications for the Origin of the Ridge. <i>Journal of Geophysical Research: Planets</i> , <i>125</i> (10), e2019JE006319. https://doi.org/10.1029/2019JE006319
991	Thorpe, M. T., Hurowitz, J. A., & Dehouck, E. (2019). Sediment geochemistry and mineralogy
992	from a glacial terrain river system in southwest Iceland. <i>Geochimica et Cosmochimica</i>
993	<i>Acta</i> , 263, 140–166. https://doi.org/10.1016/j.gca.2019.08.003
994	Thorpe, M. T., Bristow, T. F., Rampe, E. B., Grotzinger, J. P., Fox, V. K., Bennett, K. A., et al.
995	(2021). The Mineralogy and Sedimentary History of the Glen Torridon Region, Gale
996	Crater, Mars. In 52nd Lunar and Planetary Science Conference (p. 1519). Retrieved from
997	https://ui.adsabs.harvard.edu/abs/2021LPI52.1519T
998 999 1000 1001	Tosca, N. J., McLennan, S. M., Clark, B. C., Grotzinger, J. P., Hurowitz, J. A., Knoll, A. H., et al. (2005). Geochemical modeling of evaporation processes on Mars: Insight from the sedimentary record at Meridiani Planum. <i>Earth and Planetary Science Letters</i> , 240, 122–148. https://doi.org/10.1016/j.epsl.2005.09.042
1002 1003 1004 1005 1006	 Treiman, A. H., Bish, D. L., Vaniman, D. T., Chipera, S. J., Blake, D. F., Ming, D. W., et al. (2016). Mineralogy, provenance, and diagenesis of a potassic basaltic sandstone on Mars: CheMin X-ray diffraction of the Windjana sample (Kimberley area, Gale Crater). <i>Journal of Geophysical Research: Planets</i>, 121(1), 2015JE004932. https://doi.org/10.1002/2015JE004932
1007	Treiman, A. H., Downs, R. T., Ming, D. W., Morris, R. V., Thorpe, M. T., Hazen, R. M., et al.
1008	(2021). Possible Detection of a Jahnsite-Whiteite Group Phosphate Mineral by MSL
1009	CheMin in Glen Torridon, Gale Crater, Mars. In <i>52nd Lunar and Planetary Science</i>
1010	<i>Conference</i> (p. 1200). Retrieved from
1011	https://ui.adsabs.harvard.edu/abs/2021LPI52.1200T
1012	VanBommel, S. J., Gellert, R., Berger, J. A., Campbell, J. L., Thompson, L. M., Edgett, K. S., et
1013	al. (2016). Deconvolution of distinct lithology chemistry through oversampling with the
1014	Mars Science Laboratory Alpha Particle X-Ray Spectrometer. <i>X-Ray Spectrometry</i> ,
1015	45(3), 155–161. https://doi.org/10.1002/xrs.2681
1016	VanBommel, S. J., Gellert, R., Berger, J. A., Thompson, L. M., Edgett, K. S., McBride, M. J., et
1017	al. (2017). Modeling and mitigation of sample relief effects applied to chemistry
1018	measurements by the Mars Science Laboratory Alpha Particle X-ray Spectrometer. <i>X-Ray</i>
1019	<i>Spectrometry</i> , 46(4), 229–236. https://doi.org/10.1002/xrs.2755
1020	 VanBommel, S. J., Gellert, R., Boyd, N. I., & Hanania, J. U. (2019). Empirical simulations for
1021	further characterization of the Mars Science Laboratory Alpha Particle X-ray
1022	Spectrometer: An introduction to the ACES program. <i>Nuclear Instruments and Methods</i>
1023	<i>in Physics Research Section B: Beam Interactions with Materials and Atoms</i> , 441, 79–87.
1024	https://doi.org/10.1016/j.nimb.2018.12.040
1025	Vaniman, D. T., Bish, D. L., Ming, D. W., Bristow, T. F., Morris, R. V., Blake, D. F., et al.
1026	(2014). Mineralogy of a Mudstone at Yellowknife Bay, Gale Crater, Mars. <i>Science</i> ,
1027	343(6169), 1243480. https://doi.org/10.1126/science.1243480
1028	Wiens, R. C., Maurice, S., Lasue, J., Forni, O., Anderson, R. B., Clegg, S., et al. (2013). Pre-
1029	flight calibration and initial data processing for the ChemCam laser-induced breakdown

- 1030spectroscopy instrument on the Mars Science Laboratory rover. Spectrochimica Acta1031Part B: Atomic Spectroscopy, 82, 1–27.
- Williams, R. M. E., Grotzinger, J. P., Dietrich, W. E., Gupta, S., Sumner, D. Y., Wiens, R. C., et
 al. (2013). Martian Fluvial Conglomerates at Gale Crater. *Science*, *340*(6136), 1068–
 1072. https://doi.org/10.1126/science.1237317
- 1035 Wood, W. W., & Low, W. H. (1988). Solute geochemistry of the Snake River plain regional
 1036 aquifer system, Idaho and eastern Oregon (Report No. 1408D) (p. 91).
 1037 https://doi.org/10.3133/pp1408D
- Yen, A. S., Gellert, R., Schröder, C., Morris, R. V., Bell, J. F., Knudson, A. T., et al. (2005). An
 integrated view of the chemistry and mineralogy of martian soils. *Nature*, 436(7047), 49–
 54. https://doi.org/10.1038/nature03637
- Yen, A. S., Ming, D. W., Vaniman, D. T., Gellert, R., Blake, D. F., Morris, R. V., et al. (2017).
 Multiple stages of aqueous alteration along fractures in mudstone and sandstone strata in
 Gale Crater, Mars. *Earth and Planetary Science Letters*.
- 1044 https://doi.org/10.1016/j.epsl.2017.04.033
- Yen, A. S., Morris, R. V., Ming, D. W., Schwenzer, S. P., Sutter, B., Vaniman, D. T., et al.
 (2021). Formation of Tridymite and Evidence for a Hydrothermal History at Gale Crater, Mars. *Journal of Geophysical Research: Planets*, *126*(3), e2020JE006569.
- 1048 https://doi.org/10.1029/2020JE006569



JGR-Planets

Supporting Information for

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

J. A. Berger^{1*}, P. L. King², R. Gellert³, B. C. Clark⁴, V. A. Flood⁵, M. A. McCraig³, D. W. Ming¹, C. D. O'Connell-Cooper⁶, M. E. Schmidt⁷, L. M. Thompson⁶, S. J. V. VanBommel⁸, B. Wilhelm³, A. S. Yen⁹

¹NASA Johnson Space Center; ²Research School of Earth Sciences, The Australian National University, Canberra, AUS;
 ³University of Guelph, Guelph, CAN; ⁴Space Science Institute, Boulder, CO, USA; ⁵University of Toronto, Toronto, CAN;
 ⁶University of New Brunswick, Fredericton, CAN; ⁷Brock University, St. Catharines, CAN; ⁸Washington University, St. Louis, USA;
 ⁹JPL-Caltech, Pasadena, USA; *Corresponding author jeffrey.a.berger@nasa.gov

Contents of this file

Explanations for Data Set S1 Tables S1 to S6 Figures S1 to S4 References

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".

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., _raster1, _raster2) 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 ($SO3 > 15wt\%$) 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_measureme nt	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.

Explanation of columns in Data Set S1

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.
A12O3	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.

^ahttps://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."

	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_2O_5	0.84	0.05	15	0.3
Cr_2O_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

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

^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).

Fig. 3 panel	Solª	Target name	Camera	Data product/sequence number	Image adjustments ^b	MAHLI focus motor count	MAHLI standoff (cm)	MAHLI resolution ^c (µm/pixel)	Image credit
а	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_3 188_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_0 000_UNCORM1	Stretch 2%				JPL- Caltech
f	1727	Jones Marsh	MAHLI	1727MH0001530000404803R00 1727MH0001530000404805R00 1727MH0001530000404807R00	Stretch RGB	13862	5	35	MSSS
g	2664	Dunbartonsh ire refined	Mastcam	Sequence mcam13965	Stretch RGB				MSSS
h	2690	Dunbartonsh ire refined	MAHLI	2690MH0001900011001873C00	Stretch RGB	13017	25	100	MSSS
i	2857	Ayton	MAHLI	2857MH0007060011003305C00	Stretch RGB	13019	25	100	MSSS

Table S2: Table of image metadata for Figure 3

^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: Summar	v of 21 measurement	ts of 12 targets wit	:h 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	Р	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	Р	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	Р	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		Р	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	Р	1.24 ± 0.03	2.49 ± 0.14	1.61 ± 0.04	16.14 ± 0.20	2171 ± 70
1679	Maple_Spring	Nodules		Р	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		Р	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	Р	1.15 ± 0.03	2.38 ± 0.14	1.72 ± 0.03	16.19 ± 0.20	2072 ± 65
2906	Groken_tailings	Nodules		Р	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		Р	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.

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)						
HCO3 ⁻	0.1	Mean SRB (Wood & Low, 1988) is 222 mg/L	Lowered from 222 mg/L to suppress carbonate precipitation					
Cl ⁻	10 (Charge balance)	(Newcomb, 1972) ^b	(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 ⁻					
SO_4^{2-}	67	(Wood & Low, 1988)	Average sulfate for CRBG is lower: 20 mg/L (Newcomb, 1972) ^b					
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) ³ mean of 51 µg/L					
Mn ²⁺	0.010	(Wood & Low, 1988)	Median of analyses above detection limit stated as both 10 μ m/L and 1 μ m/L (57% of total analyses). Consistent with (Steinkampf & Hearn, 1996)° mean of 15 μ g/L					
HPO42-	0.13	(Newcomb, 1972)	"Common range" reported is 0.02 to 0.30 mg/L in CRBG					

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

^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).

Step	Ionic strength (molal)	Dissolv ed solids (mg/kg sol'n)	рН	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)
			А	dapted fror	n Snake R	iver Plains	Basalt Aqu	ifers (SRPE	3)			
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
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

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

^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: Descri	ption of sample	e 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 \sim 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 $< 150 \ \mu m$	Postsieve	Sample processed by SA/SPaH, sieved to $<150 \mu m$, 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 μ m sieve, and dumped on the ground. The targets include "presieve" in the name
Sieved 150-1000 µm	Sieve150µm-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_a). 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_a 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_a peaks are denoted, and unlabeled peaks include the K_β lines of Cl, Ca, Ti, Fe and Ni as well as the Ar K_a 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 \pm 0.04 wt%) is indicated in red.



Figure S4: MnO versus (a) P_2O_5 , (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.

References

- Drever, J. I. (1997). *The Geochemistry of Natural Waters: Surface and Groundwater Environments* (3rd ed.). Prentice Hall.
- Gellert, R., & Clark, B. C. (2015). In situ compositional measurements of rocks and soils on NASA's Mars rovers with the alpha-particle X-ray spectrometer (APXS). *Elements*, *11*, 39–44.
- Gellert, R., Rieder, R., Brückner, J., Clark, B. C., Dreibus, G., Klingelhöfer, G., et al. (2006). Alpha Particle X-Ray Spectrometer (APXS): Results from Gusev crater and calibration report. *Journal of Geophysical Research*, 111(E02S05). https://doi.org/200610.1029/2005JE002555
- Langmuir, D., & Whittemore, D. O. (1971). Variations in the Stability of Precipitated Ferric Oxyhydroxides. In *Nonequilibrium Systems in Natural Water Chemistry* (Vol. 106, pp. 209–234). AMERICAN CHEMICAL SOCIETY. https://doi.org/10.1021/ba-1971-0106.ch008
- Newcomb, R. C. (1972). Quality of the Ground Water in Basalt of the Columbia River Group, Washington, Oregon, and Idaho (Water supply paper No. 1999- N) (p. 71). U. S. Geological Survey.
- Steinkampf, W. C., & Hearn, P. P. (1996). *Ground-Water Geochemistry of the Columbia Plateau Aquifer System, Washington, Oregon, and Idaho* (Open-File Report No. 95–467) (p. 67). Tacoma, Washington: U. S. Geological Survey.
- VanBommel, S. J., Gellert, R., Berger, J. A., Yen, A. S., & Boyd, N. I. (2019). Mars Science Laboratory Alpha Particle X-ray spectrometer trace elements: Situational sensitivity to Co, Ni, Cu, Zn, Ga, Ge, and Br. *Acta Astronautica*, *165*, 32–42. https://doi.org/10.1016/j.actaastro.2019.08.026
- Wood, W. W., & Low, W. H. (1988). Solute geochemistry of the Snake River plain regional aquifer system, Idaho and eastern Oregon (Report No. 1408D) (p. 91). https://doi.org/10.3133/pp1408D