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1 **X-ray amorphous components in sedimentary rocks of Gale crater, Mars: Evidence**  
2 **for ancient formation and long-lived aqueous activity**

3  
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19 **Key Points:**

- 20
- 21 • X-ray amorphous abundances are positively correlated with SiO<sub>2</sub> content, and amorphous  
SiO<sub>2</sub> and FeO<sub>T</sub> contents are anticorrelated.
  - 22 • X-ray amorphous SiO<sub>2</sub> and FeO<sub>T</sub> contents in Gale crater sedimentary rocks largely  
23 represent multiple aqueous processes occurring over time.
  - 24 • It is unclear how such metastable materials have persisted for billions of years.  
25

## 26 **Abstract**

27       The CheMin instrument on the Mars Science Laboratory rover *Curiosity* detected  
28 ubiquitous high abundances (~15-70 wt%) of X-ray amorphous components (AmCs) in ancient  
29 sedimentary rocks of Gale crater. Mechanisms and timing of formation for the AmCs are poorly  
30 constrained, and could include volcanic, impact, or aqueous processes. We explore trends in  
31 AmC composition and abundance, and look for systematic compositional variation between sites  
32 within Gale crater. AmC compositions were estimated indirectly based on bulk chemistry and the  
33 nature and abundance of the crystalline phases for 19 sedimentary rock samples. AmC  
34 abundances positively correlate with AmC SiO<sub>2</sub> contents, and a mixing relationship appears to  
35 exist between SiO<sub>2</sub>-rich and FeO<sub>T</sub>-rich AmC endmembers. Endmember compositions are  
36 inconsistent with volcanic or impact glass alone, and so we conclude that the SiO<sub>2</sub> and FeO<sub>T</sub>  
37 contents formed largely through aqueous processes. Cross-cutting relationships and geologic  
38 context provide evidence that the most SiO<sub>2</sub>-rich AmCs observed in Gale crater thus far may  
39 result from interactions with localized fluids during late diagenesis. AmCs with moderate to low  
40 SiO<sub>2</sub> contents likely formed earlier (before or soon after the deposition of sediments). Thus, the  
41 AmC SiO<sub>2</sub> and FeO<sub>T</sub> contents in Gale crater rocks represent mixtures of sedimentary materials  
42 formed over most of the sedimentary history of Gale crater, starting before the first sediments  
43 were deposited in the crater (late Noachian), and ending well after the youngest sediments were  
44 lithified (at least mid Hesperian). However, it remains unclear how these metastable minerals  
45 have persisted through billions of years of diagenesis in Gale crater sediments.

## 46 **Plain Language Summary**

47       The CheMin instrument on the Mars Science Laboratory rover *Curiosity* detected  
48 ubiquitous high abundances (~15-70 weight %) of amorphous materials in ancient sedimentary  
49 rocks of Gale crater. It is uncertain what geologic processes these materials represent (volcanic  
50 eruptions, impacts, or interactions with water), and when these materials were formed. Here we  
51 explore these possible formation mechanisms and their timing by estimating the chemical  
52 compositions of the amorphous materials, and looking for trends and variations in their  
53 compositions along the rover traverse. We find that amorphous iron- and silica-rich materials  
54 formed mostly through interactions with water, and likely represent mixtures of chemical  
55 weathering products, chemical sediments, and cements that accumulated over time. We also find  
56 that some of the amorphous materials formed early on in the history of the crater, while others  
57 formed long after sediments were deposited and turned into rock, indicating that water persisted  
58 at Gale crater for ~1 billion years. On Earth, it is thought that amorphous materials are readily  
59 converted into more crystalline materials in the presence of water, but it is unclear why this is not  
60 the case for Mars.

## 61 **1 Introduction**

62       The Mars Science Laboratory (MSL) rover *Curiosity* has examined hundreds of  
63 stratigraphic meters of ancient fluviolacustrine and eolian sedimentary rocks in Gale crater  
64 (137.4°E, -4.6°N) since landing in August 2012 (Grotzinger et al., 2015; Figure 1). Among the  
65 most puzzling discoveries is the detection of high abundances (~15-70 wt%) of X-ray amorphous  
66 components (AmCs) in all sedimentary materials analyzed, including both unconsolidated eolian  
67 sediments and ancient (~3.5 billion-year-old) sedimentary rocks (Rampe et al., 2020a and  
68 references therein). Addressing the mechanisms and timing of formation of these components is  
69 critical for understanding Martian sedimentary processes, but they remain largely unconstrained

70 (McLennan et al., 2019). Amorphous materials could include primary glass deposited by fluvial  
71 or eolian processes (e.g., ash fall, impact glasses), secondary alteration products, chemical  
72 precipitates from surface or pore waters, and/or post-depositional diagenetic products. For some  
73 of the sampling locations, evolved gas analyses measured by the Sample Analysis at Mars  
74 (SAM) instrument show wide volatile release temperatures for H<sub>2</sub>O and SO<sub>2</sub> that have been  
75 partially attributed to X-ray amorphous materials, suggesting that at least some fraction of the X-  
76 ray amorphous components formed through aqueous processes (Leshin et al., 2013; Sutter et al.,  
77 2017).

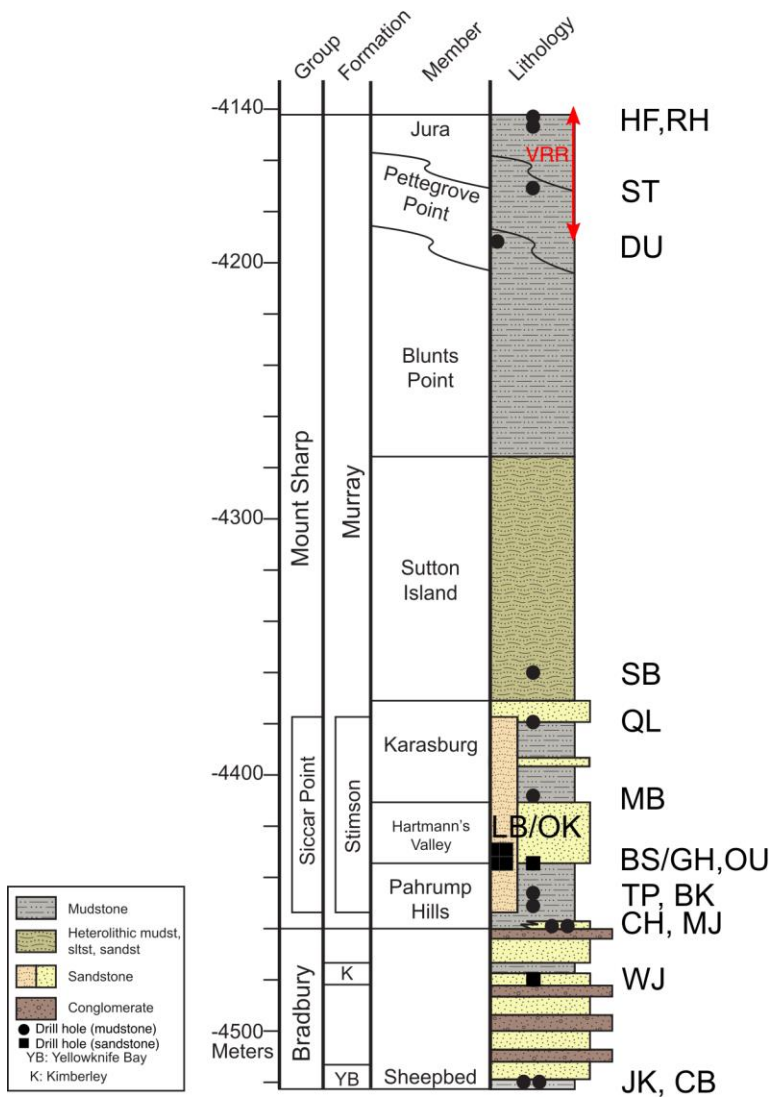
78 AmCs were detected with the CheMin X-ray diffractometer (XRD) (Blake et al., 2012).  
79 CheMin analyses are restricted to sieved sediment or powdered drill fines. As of December 2019  
80 (sol 2300), CheMin data are available for 19 sedimentary rock samples along the rover traverse,  
81 representing each of the major stratigraphic units encountered (Figure 1).

82 Such high abundances of X-ray amorphous materials in 3-4 Gy old and diagenetically  
83 altered sedimentary rocks is an unexpected discovery, as amorphous and nanocrystalline  
84 materials are thermodynamically metastable and are susceptible to particle coarsening processes  
85 that convert amorphous and nanocrystalline materials to more stable minerals and larger crystals  
86 (e.g., Steefel and Van Cappellen, 1990; De Yoreo et al., 2015). Therefore, it is widely thought  
87 that they should not be found in high abundance in sedimentary rocks, which undergo diagenesis  
88 before, during, and after lithification (Mack et al., 1993; Harsh, 2005). For example, the oldest  
89 known occurrences of opaline silica are Cretaceous in age, but it is exceedingly rare to find  
90 opaline silica in terrestrial sedimentary rocks older than a few million years (e.g., Tosca and  
91 Knoll, 2009). Yet, amorphous and nanocrystalline weathering products are significant  
92 components (~10-30 wt%) of 30-50 My old Mars-analog paleosols (Smith et al., 2018),  
93 indicating that this general conclusion might not always hold true, and that some settings allow  
94 amorphous materials to be preserved in Earth sediments for at least 10s to 100s of millions of  
95 years.

96 Previous workers estimated bulk AmC compositions in Gale crater through mass balance  
97 calculations that combine bulk sample geochemistry from the Alpha Particle X-ray Spectrometer  
98 (APXS; Gellert et al., 2015) with CheMin-derived mineral stoichiometries and abundances  
99 (Blake et al., 2013; Dehouck et al., 2014; Vaniman et al., 2014; Morris et al., 2016; Treiman et  
100 al., 2016; Achilles et al., 2017, 2020; Rampe et al., 2017; Yen et al., 2017). These results show  
101 that AmC compositions vary between sampling locations, particularly in SiO<sub>2</sub> and FeO<sub>T</sub>  
102 abundance. However, to date, no study has explored if there are any trends with AmC  
103 composition and abundance, or explored if there is systematic compositional variation between  
104 sedimentary units in Gale crater. Here we focus on AmC SiO<sub>2</sub> and FeO<sub>T</sub> concentrations and  
105 examine how the proportions of these two oxides are related to AmC abundances and  
106 stratigraphic position. We then place observations into the context of our current understanding  
107 of the geologic history of Gale crater.

## 108 **2 Geologic Overview**

109 The ~154 km diameter impact basin Gale crater is located near the equator of Mars, on  
110 the crustal dichotomy boundary between the northern lowlands and the southern highlands. As of  
111 sol (one day on Mars) 2300, MSL had driven over 20 km laterally and gained 380 m of  
112 elevation. Almost all rocks that MSL has encountered have been sedimentary, and the strata are  
113 generally flat-lying such that elevation can be used as a proxy for thickness of the stratigraphic



**Figure 1.** Stratigraphic column of Gale crater (up to sol 2300). Drill holes: JK–John Klein, CB–Cumberland, WJ–Windjana, CH–Confidence Hills, MJ–Mojave, TP–Telegraph Peak, BK–Buckskin, OU–Oudam, MB–Marimba, QL–Quela, SB–Sebina, DU–Duluth, ST–Stoer, HF–Highfield, RH–Rockhall, BS–Big Sky, OK–Okoruso, GH–Greenhorn, LB–Lubango. Stratigraphic position of Vera Rubin ridge (VRR) is shown near the top. Figure credit: the MSL Science Team sed/strat working group.

114 section. Along its traverse, the rover has observed and investigated approximately 380 m of  
 115 sedimentary rock stratigraphy comprising the crater plains and the central mound Mount Sharp  
 116 (Aeolis Mons) that rises ~5 km high from the floor of Gale crater (e.g., Grotzinger et al., 2014,  
 117 2015).

118 The Gale crater impact event occurred ~3.6 to 3.8 Gy ago during the late Noachian/early  
 119 Hesperian epochs (Thomson et al., 2011). Based on careful documentation of the lithologies  
 120 encountered along the rover traverse, the rock-forming sediments were supplied to Gale crater by

121 a combination of fluvial, lacustrine, and eolian processes (Figure 1; Edgar et al., 2017; Williams  
122 et al., 2013; Grotzinger et al., 2014, 2015; Rivera-Hernández et al., 2020; Stack et al., 2019;  
123 Banham et al., 2018). It is possible that the entire crater was filled with sediments by the late  
124 Noachian/early Hesperian before being eroded through eolian processes (Malin and Edgett,  
125 2000; Le Deit et al., 2013; Grotzinger et al., 2015). Further sedimentation, evidenced by the  
126 unconformable eolian Stimson formation (Watkins et al., 2015, Banham et al., 2018) was  
127 followed by additional eolian erosion to form the modern crater topography, likely approaching  
128 the modern topography approximately 3 billion years ago (Grant et al., 2014).

129 Multiple diagenetic events are recorded in the sedimentary rocks in Gale crater, but other  
130 than a K-Ar age date <3 Ga (possibly as young as ~2.1 Ga) for likely jarosite in a single drill  
131 hole location (Martin et al., 2017), the timeframes for these processes are poorly constrained.  
132 Buried sediments underwent the diagenetic process of lithification, which includes porosity  
133 reduction through compaction and cementation (Worden and Burley, 2003), and contain  
134 evidence for more localized early diagenetic processes including concretions, desiccation and  
135 syneresis cracks, and lenticular crystal pseudomorphs (Siebach et al., 2014; Stack et al., 2014;  
136 Stein et al., 2018; Sun et al., 2019; Blaney et al., 2014; Kah et al., 2018). Extensive networks of  
137 Ca-sulfate veins and fracture-associated alteration halos suggest that diagenetic fluids continued  
138 to circulate through the rocks long after lithification (e.g. Nachon et al., 2014, 2017; Frydenvang  
139 et al., 2017; Yen et al., 2017; Gabriel et al., 2019; Kronyak et al., 2019).

140 At the time of this study, MSL has examined three major stratigraphic groups (Figure 1).  
141 The Bradbury group rocks, comprising mostly fluviodeltaic sediments, make up part of the crater  
142 floor deposits, and are interpreted to be the oldest rocks examined by the rover (Grotzinger et al.,  
143 2015). CheMin examined three Bradbury group drill hole locations: two lacustrine mudstones in  
144 the Yellowknife Bay formation, John Klein (JK) and Cumberland (CB) (see Figure 1 caption for  
145 sample name abbreviations used throughout the text), and one sandstone consisting of reworked  
146 deltaic and eolian sediments located in the Kimberley formation, Windjana (WJ) (Rice et al.,  
147 2017; Vaniman et al., 2014; Treiman et al., 2016; Morrison et al., 2018). The Bradbury group  
148 rocks likely had Fe-rich olivine tholeiitic sediment sources (JK and CB) with the possibility of an  
149 additional alkali-feldspar-rich sediment source in some locations (WJ) (e.g., Treiman et al.,  
150 2016; Edwards et al., 2017; Siebach et al., 2017; Bedford et al., 2018; Payré et al., 2020).

151 As a whole, the Mount Sharp group overlies the Bradbury group, and all of the Mount  
152 Sharp group rocks examined by the rover are thought to be younger than those examined in the  
153 Bradbury group (Grotzinger et al., 2015). As of sol 2300, CheMin had analyzed 12 drill hole  
154 locations within the Mount Sharp group (Morris et al., 2016; Rampe et al., 2017, 2020b; Achilles  
155 et al., 2020). Most of these rocks are fluviolacustrine mudstones and fine-grained sandstones  
156 (e.g., Rivera-Hernández et al., 2020) that have geochemical compositions distinct from  
157 sediments in the Bradbury group (Berger et al., 2020; Thompson et al., 2020) indicating a change  
158 in dominant sediment sources. Mount Sharp group sediment compositions are mostly  
159 fractionated, relatively SiO<sub>2</sub>-rich subalkaline basalt (Bedford et al., 2018). The Mount Sharp  
160 group also includes Vera Rubin ridge (VRR; between ~ -4190 and -4140 m), a topographic ridge  
161 that shows strong spectral signatures of hematite from orbit and the ground, and is interpreted to  
162 have experienced substantial diagenetic alteration relative to the surrounding units (e.g., Fraeman  
163 et al., 2020; David et al., 2020; Horgan et al., 2020; L'Haridon et al., 2020; Rampe et al., 2020b).

164 Both the Bradbury and Mount Sharp groups were buried, lithified, and later exhumed by  
165 eolian erosion (Malin and Edgett, 2000; Grotzinger et al., 2015; Day et al., 2016). Some time

166 after erosion, the subaerial sand dune sediments of the Siccar Point group were deposited on  
167 some sections of the Mount Sharp group (Figure 1). The eolian dunes were then buried and  
168 lithified, creating an unconformable surface between parts of the Mount Sharp group and the  
169 Siccar Point group (Watkins et al., 2016; Banham et al., 2018). CheMin analyzed four drill holes  
170 within the Siccar Point group: two within parent bedrock, Big Sky (BS) and Okoruso (OK), and  
171 two within light-toned alteration “halos” surrounding central fractures, Greenhorn (GH) and  
172 Lubango (LB) (Yen et al., 2017). The sediments for the Siccar Point group rocks have a  
173 subalkaline basaltic composition, and the Siccar Point and Bradbury groups are hypothesized to  
174 share a similar local sediment source (Bedford et al., 2020). The fracture-associated alteration  
175 halos are silica-enriched zones ~50 cm wide that crosscut both the Mount Sharp and overlying  
176 Siccar Point group rocks (Frydenvang et al., 2017; Yen et al., 2017). These alteration halos have  
177 been interpreted as late diagenetic features that represent either chemical precipitates  
178 (Frydenvang et al., 2017) or leaching residue (Yen et al., 2017), and may have formed as a result  
179 of multiple fluid episodes (Yen et al., 2017; Hausrath et al., 2018).

180

### 181 **3 Materials and Methods**

#### 182 3.1 Calculating X-ray amorphous component compositions

183 AmC compositions were determined using mass balance calculations for all rock samples  
184 analyzed in the first ~2300 sols of the mission (Figure 1). We used methods developed by  
185 Dehouck et al. (2014) and validated using analog samples by Smith et al. (2018), in which we  
186 input bulk sample geochemistry from APXS (representing crystalline + amorphous  
187 compositions), crystalline mineral abundances and compositions from CheMin, and AmC  
188 abundance from CheMin (see Supplemental Material for input details). The crystalline  
189 component composition was subtracted from bulk sample composition so what remained was an  
190 estimate of the bulk AmC composition, with several caveats listed below. We performed two  
191 mass balance calculations for each sample: (1) a “best estimate” composition, named as such  
192 because only the best estimate abundance for each mineral was considered during the calculation  
193 (i.e., uncertainties on mineral abundances were not considered) resulting in only one AmC  
194 composition for each sample, (2) a range of possible AmC compositions using mineral  
195 abundance uncertainties (see Dehouck et al., 2014 for details). Here we focused on “best  
196 estimate” compositions, and note that the ranges for AmC SiO<sub>2</sub> and FeO<sub>T</sub> were mostly < ±5 wt%  
197 (Table S1). Compositions were reported as oxide wt% in 100% AmC (Table S2), as opposed to  
198 wt% oxide in the amorphous state in 100% sample (crystalline + AmC), because we are  
199 interested in how the composition (SiO<sub>2</sub> and FeO<sub>T</sub> content) of the amorphous material changes  
200 between locations.

201 APXS frequently acquires multiple bulk sample geochemistry measurements of drilled  
202 samples (e.g., drill tailings, discard pile). We used measurements of post-sieve dump piles when  
203 available or fines dumped from the drill bit to be most consistent with samples measured by  
204 CheMin (Table S3). Crystalline mineral abundances and compositions are from CheMin XRD  
205 pattern Rietveld refinements (Morrison et al., 2018; Achilles et al., 2020; Rampe et al., 2020b;  
206 Tables S4-5). Opal-CT, identified in four samples (TP, BK, OU, HF; Rampe et al., 2020a; see  
207 Figure 1 for sample name abbreviations), was included in the AmC. Clay minerals were included  
208 in the crystalline component, and abundances and compositions were based on FULLPAT  
209 analyses and XRD pattern comparisons (Tables S6-S7; Bristow et al., 2015, 2018; Baudat et al.,

210 1992; Brigatti, 1983; Novák and Čížek, 1978; Post, 1984; Treiman et al., 2014). Lastly, we used  
211 either the AmC abundance derived from FULLPAT XRD analyses (Morrison et al., 2018;  
212 Achilles et al., 2020; Rampe et al., 2020b) or the minimum AmC abundance needed to produce a  
213 chemically realistic AmC composition if the XRD-derived abundance resulted in negative AmC  
214 oxide abundances (Table S1).

215 Caveats for interpreting mass balance calculation results include: (1) elements in  
216 crystalline phases below the CheMin XRD detection limit of ~1 wt.% (e.g., Cr in chromite, Ti in  
217 anatase) are allocated to the AmC composition; (2) minor element substitutions not accounted  
218 for in ideal structure formulas for crystalline minerals (e.g., Al, Ti, Cr, Mn, and Na in pyroxenes;  
219 K in plagioclase) are also allocated to the AmC composition; (3) when present and poorly  
220 constrained, complex clay mineral compositions can affect the accuracy of AmC compositions  
221 (Dehouck et al., 2014; Smith et al., 2018). These potential compositional artifacts add additional,  
222 but not readily quantifiable, uncertainties, especially for elements at relatively low  
223 concentrations in the amorphous component, including Ti, Al, Mn, Na, K, Cl, P, and Cr.  
224 Accordingly, this study focuses on SiO<sub>2</sub> and FeO<sub>T</sub> because their concentrations in the AmC are  
225 relatively high, so uncertainties on abundances, even if a small proportion resides in unaccounted  
226 for crystalline phases, are relatively low, and they are both essential compositional constituents  
227 in several of the proposed amorphous phases.

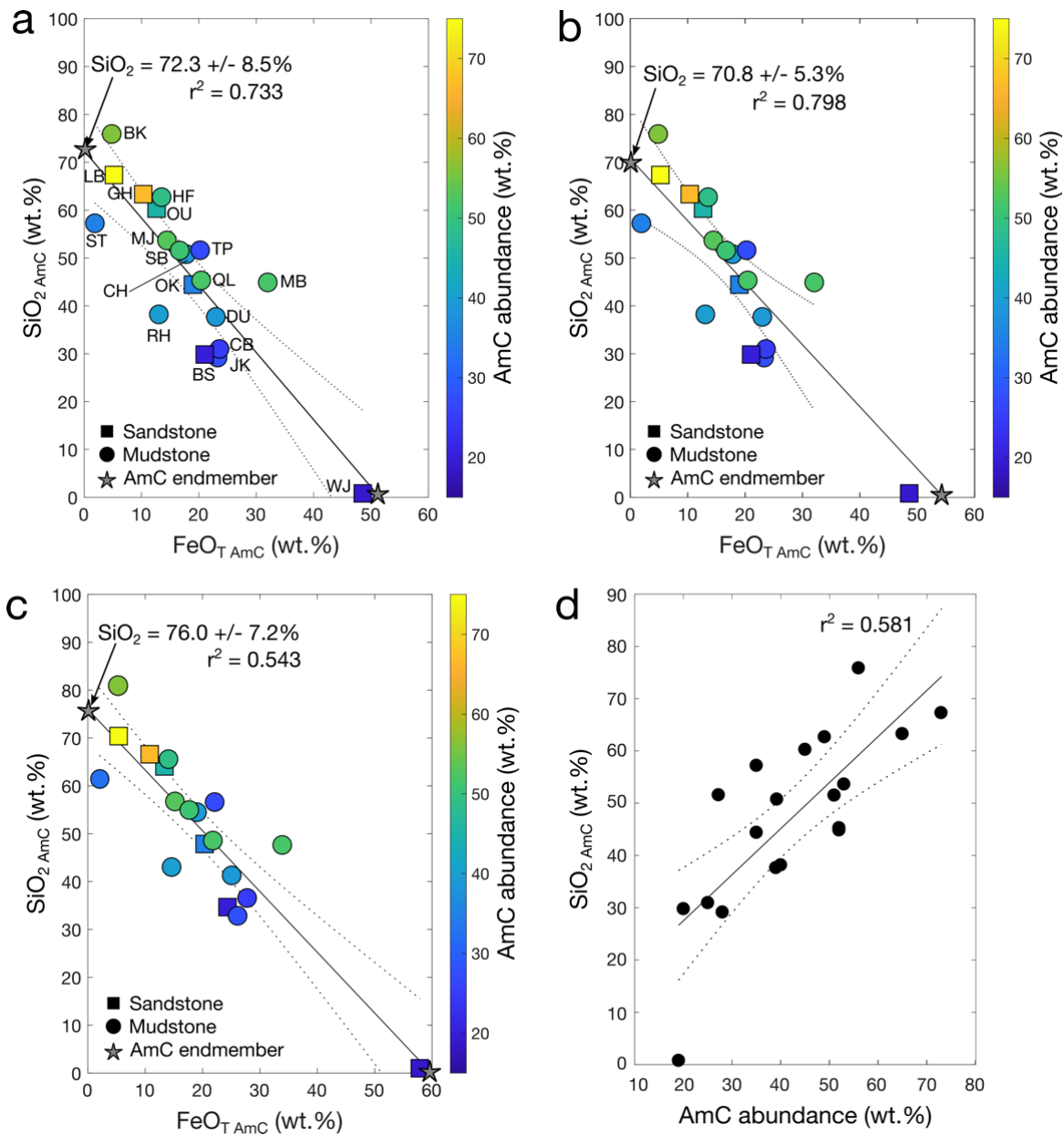
## 228 **4 Results**

229 Calculated SiO<sub>2</sub> and FeO<sub>T</sub> contents (wt% oxide in AmC) are compared to AmC  
230 abundances in Figures 2a and 2d. Samples with high AmC abundances tend to have SiO<sub>2</sub>-rich  
231 AmCs, and samples with low AmC abundances tend to have FeO<sub>T</sub>-rich AmCs. This correlation  
232 is evidence for a mixing relationship between hypothetical SiO<sub>2</sub>-rich and FeO<sub>T</sub>-rich AmC  
233 endmembers.

234 Linear regression provides an estimate of the composition of the hypothetical SiO<sub>2</sub>-  
235 endmember (i.e., intercept at FeO<sub>T</sub> = 0 wt%), which is not pure SiO<sub>2</sub>, but 72.3% ( $\pm$  8.5%) SiO<sub>2</sub> at  
236 2-standard error with an  $r^2$  value of 0.733. This should be considered a minimum SiO<sub>2</sub> wt%  
237 value, because ~2-7 wt% of the oxides in each sample allocated to the AmC composition could  
238 actually be present in the crystalline components (TiO<sub>2</sub>, MnO, Cr<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Cl; Table S2). By  
239 subtracting these oxides from each amorphous component, and renormalizing to 100%, we  
240 estimate that the SiO<sub>2</sub> wt% value could actually be at high as ~76.0 ( $\pm$  7.2%) SiO<sub>2</sub> at 2-standard  
241 error with an  $r^2$  value of 0.798 (Figure 2c). The improved fit could also be indicative of a better  
242 SiO<sub>2</sub> composition estimate. Combined, these estimates (including the 2-standard errors) indicate  
243 a SiO<sub>2</sub>-rich endmember that is between ~64 and 83 wt% SiO<sub>2</sub>. No single oxide shows a positive  
244 correlation with AmC SiO<sub>2</sub>, so several different constituents are responsible for the impurity of  
245 the SiO<sub>2</sub>-endmember.

246 The linear regression in Figure 2 also provides a composition for the hypothetical FeO<sub>T</sub>-  
247 endmember, which is ~52% FeO<sub>T</sub> (at SiO<sub>2</sub> = 0 wt%). It might seem that this composition is  
248 predominantly constrained by the most FeO<sub>T</sub>-rich AmC drill hole location (WJ), which has a  
249 composition very different from all other AmCs. However, if the linear regression is forced to  
250 ignore the WJ location (Figure 2b), the change to the hypothetical FeO<sub>T</sub>-endmember composition  
251 is minimal (~55% FeO<sub>T</sub>). Similar to the AmC SiO<sub>2</sub>, AmC FeO<sub>T</sub> shows no strong positive  
252 correlation with any single oxide, and so several different constituents are responsible for the  
253 impurity of the FeO<sub>T</sub>-endmember.

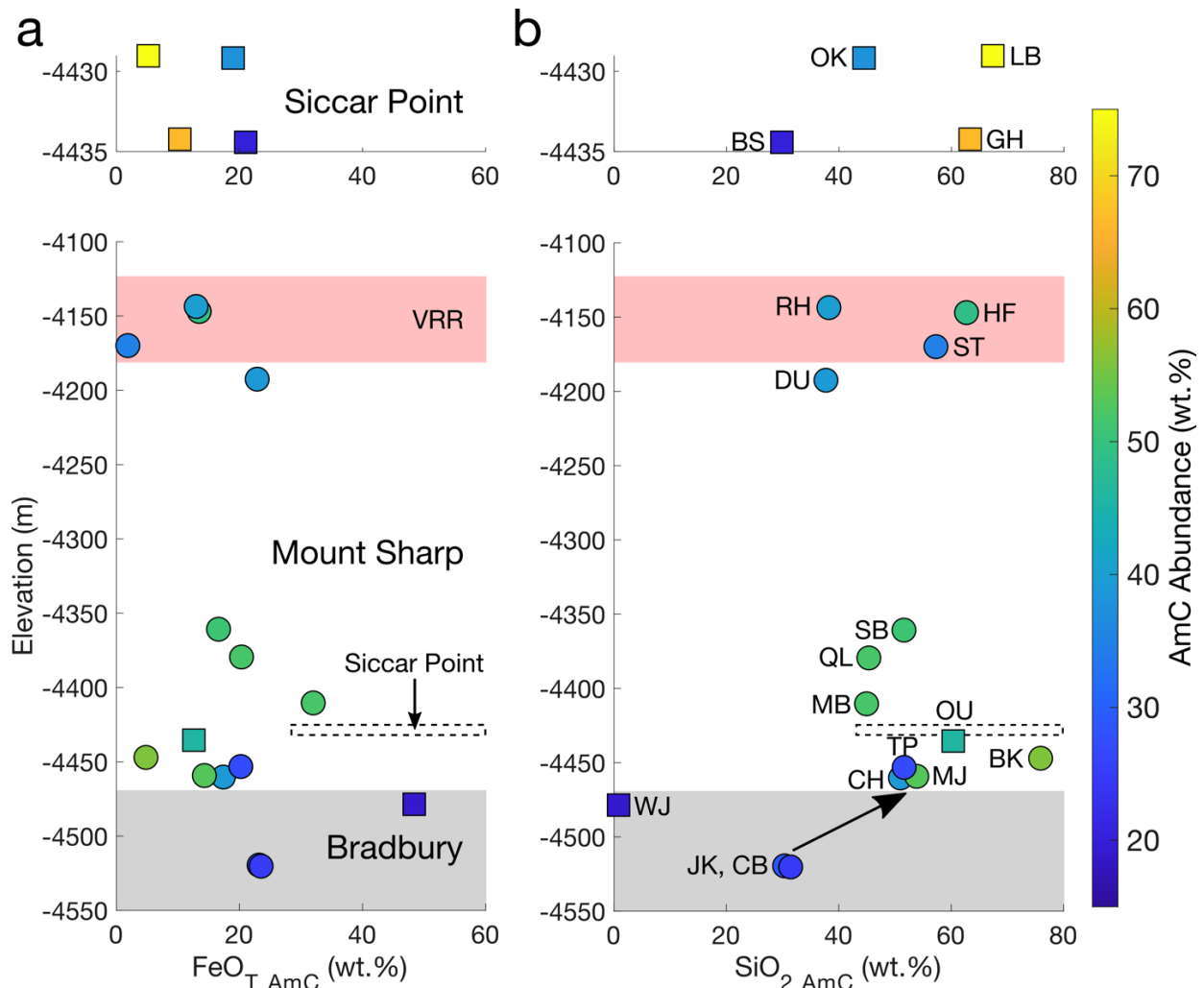


Figure 3 shows stratigraphic variation in AmC abundance and FeO<sub>T</sub> and SiO<sub>2</sub> contents

**Figure 2.** (a-c) SiO<sub>2</sub> vs. FeO<sub>T</sub> wt% in AmC for drill hole sites listed in Figure 1. Colors represent AmC abundance used in the mass balance calculation (wt%), and symbols represent lithology shown in Figure 1. Solid lines represent the regression and dotted lines  $\pm 2$ -standard error, interpreted as an approximation to a silica mixing line between FeO<sub>T</sub>- and SiO<sub>2</sub>-rich endmembers (stars). The y-intercept provides a minimum estimate of the SiO<sub>2</sub> content of the SiO<sub>2</sub>-rich endmember. (a) Regression performed using the best estimate AmC compositions, and minor elements are included in the AmC composition. (b) Regression performed using the same data as in (a), but the WJ sample is ignored. (c) Regression performed using the best estimate AmC composition, but minor elements have been subtracted from the AmC (see text). (d) SiO<sub>2</sub> wt% in AmC vs. AmC abundance (wt%) for all drill hole sites. Solid line represents the regression and dotted lines  $\pm 2$ -standard error.

255 (wt% oxide in AmC) of drill hole sites. The Bradbury group rocks sampled by CheMin all have  
 256 relatively low AmC abundances (between ~17 and 23 wt%), low AmC SiO<sub>2</sub> (~1-30 wt%), and  
 257 high AmC FeO<sub>T</sub> (~23-51 wt%) compared to most overlying sedimentary rocks. However, the  
 258 Kimberley formation location (WJ) has much lower AmC SiO<sub>2</sub> and much higher AmC FeO<sub>T</sub>  
 259 contents than the Yellowknife Bay formation sedimentary rocks (CB and JK), consistent with the  
 260 results of Dehouck et al. (2017).

261 Although the number of Bradbury group samples is limited, there appears to be a  
 262 noticeable change in AmC properties across the Bradbury-Mount Sharp group transition as the  
 263 younger, mostly lacustrine Mount Sharp group rocks sampled by CheMin all have moderate to  
 264 high AmC abundances (between ~27 and 53 wt%), high AmC SiO<sub>2</sub> (~40-75 wt%), and low to



**Figure 3.** Plots showing stratigraphic variations in AmC FeO<sub>T</sub> (a) and SiO<sub>2</sub> (b) contents (wt%). Siccar Point group data are shown in expanded plots at the top. Symbol colors represent AmC abundances (wt%), and symbol shapes represent lithology (see Figure 2). Drill hole labels are provided in (b). Arrow in (b) points to the general increase in AmC SiO<sub>2</sub> content across the Bradbury – Mount Sharp group boundary.

265 moderate AmC FeO<sub>T</sub> (~5-24 wt%). Yet, there is some variation among the Mount Sharp group  
266 rocks with anomalous (relative to the drill hole locations stratigraphically above and below)  
267 AmC SiO<sub>2</sub> contents at BK, OU, and sedimentary rocks at VRR.

268 The youngest and unconformably overlying eolian-deposited Siccar Point group rocks  
269 analyzed by CheMin have significantly variable AmC properties due to the occurrence of the  
270 fracture-associated halos. The parent sedimentary rocks (represented by samples OK and BS)  
271 have low AmC abundances (15-20 wt%), relatively low to moderate AmC SiO<sub>2</sub> (~30-45 wt%),  
272 and moderate AmC FeO<sub>T</sub> (~19-22 wt%). In contrast, the fracture-associated halo drill sites (GH  
273 and LB) have the highest AmC abundances of all sedimentary rocks examined (65-73 wt%),  
274 high AmC SiO<sub>2</sub> (~64-67 wt%), and low AmC FeO<sub>T</sub> (~5-10 wt%).

## 275 **5 Discussion**

### 276 5.1 Fire or water?

277 X-ray amorphous materials may form through volcanic eruptions, impacts, anhydrous  
278 oxidative weathering, aqueous chemical weathering and alteration, and direct precipitation from  
279 aqueous solutions either as a primary sedimentary deposit or a diagenetic constituent, all of  
280 which are possible for the Martian surface, and all of which require water except perhaps for  
281 volcanic eruptions, impacts, and anhydrous oxidative alteration. We come to the conclusion that  
282 aqueous processes were responsible for most of the variations in AmC SiO<sub>2</sub> and FeO<sub>T</sub> in Gale  
283 crater sedimentary rocks based on the following observations and supporting arguments.

284 First, the mixing line in Figure 2 suggests that all rocks in Gale crater contain a few wt%  
285 (ST) to ~20 wt% (WJ) of the hypothetical FeO<sub>T</sub>-rich AmC endmember (e.g., the WJ rock  
286 contains 20 wt% AmC that is ~100% FeO<sub>T</sub>-rich endmember). Rocks with the lowest AmC  
287 abundances (WJ, JK, CB, BS) have the highest fractions of the FeO<sub>T</sub>-rich AmC endmember, and  
288 their AmC compositions (~20-50 wt% FeO<sub>T</sub>, ~1-30 wt% SiO<sub>2</sub>, and other elements related to  
289 amorphous material and mass balance calculation artifacts) are not consistent with volcanic or  
290 impact glass alone because they would point to an implausibly exotic chemical composition  
291 (Dehouck et al., 2014). It is unlikely that anhydrous oxidative weathering products are  
292 significantly contributing to the observed AmC because such processes in terrestrial analog  
293 environments are only surficial in nature and produce minimal amounts of amorphous materials,  
294 primarily oxidizing crystalline phases (Salvatore et al., 2013, 2019). This indicates that the FeO<sub>T</sub>-  
295 rich AmCs largely formed through aqueous processes involving the alteration of primary  
296 minerals and/or glass to precipitate the amorphous (mostly) iron- and silica-bearing material.

297 Second, the mixing line in Figure 2, along with the observation that AmC abundance  
298 increases with AmC SiO<sub>2</sub> suggests that silica-rich AmC material was added to the FeO<sub>T</sub>-rich  
299 AmC material at some locations (discussed below). The estimated silica content of this silica-  
300 rich material could be anywhere in a range from ~64 to 83 wt% SiO<sub>2</sub>, which would require  
301 dacitic to rhyolitic composition volcanic and impact glasses. Apart from the Buckskin mudstone  
302 sample, which contains tridymite and cristobalite (but not quartz) and so may have a felsic  
303 volcanic provenance component (Morris et al., 2016), and the Windjana sample, which has been  
304 shown to have a mostly trachyte sediment source (Treiman et al., 2016), bulk rock compositions  
305 and crystalline component geochemistry and mineralogy provide no evidence for such evolved

306 compositions contributing to the Gale crater sedimentary rocks studied to date. Therefore, the  
307 high-silica AmC endmember also likely resulted from aqueous processes.

308 Third, mass balance modeling used to constrain the upper limit of glass contribution to  
309 the AmCs, shows that each AmC could be comprised of between as much as 0.1 and 57 wt%  
310 (median = 10 wt%; average = 17 wt%) basaltic glass of average Martian crust composition  
311 (Taylor & McLennan, 2009) (Table S8), leaving behind significant amorphous silica and iron  
312 that are not associated with volcanic or impact glass. The maximum fraction of glass was  
313 constrained by determining the limiting oxide for each sample, where a greater glass fraction  
314 would result in that oxide being left at negative abundance in the remaining amorphous  
315 component. For most AmCs, the limiting oxide was Al<sub>2</sub>O<sub>3</sub>, but in some cases was MgO or CaO,  
316 and in one sample each, FeO<sub>T</sub> and SiO<sub>2</sub> (Table S8). Note that basaltic glass can have highly  
317 variable compositions, and so glasses with lower Al<sub>2</sub>O<sub>3</sub> (or whichever the limiting oxide) would  
318 increase the possible upper limit of glass, and glasses with higher Al<sub>2</sub>O<sub>3</sub> (or whichever the  
319 limiting oxide) would decrease the possible upper limit of glass.

## 320 5.2 Possible individual X-ray amorphous phases

321 The mass balance calculation approach provides only a bulk AmC composition, and so  
322 we use our knowledge of terrestrial X-ray amorphous materials and the geologic history of Gale  
323 crater to speculate on the possible individual phases that comprise the AmCs. X-ray amorphous  
324 FeO<sub>T</sub>- and/or SiO<sub>2</sub>-bearing materials are common components of terrestrial sediments and  
325 sedimentary rocks in the form of weathering products, chemical sediments, and diagenetic  
326 cements. All of these types of materials could be present in Gale crater, a sedimentary basin that  
327 once contained a number of rivers and lakes that were likely connected by a common ground  
328 water table (Grotzinger et al., 2015), and experienced diagenetic fluid interactions as recent as  
329  $2.12 \pm 0.36$  Ga based on K-Ar dating of likely diagenetic phases (mostly jarosite) in the Mount  
330 Sharp group (Martin et al., 2017).

331 Just like secondary minerals, the compositions and structures of X-ray amorphous  
332 materials formed through aqueous processes depend on fluid compositions, climate, and  
333 environmental conditions (Eh, pH, temperature). Iron- and silica-bearing fluids would not be  
334 difficult to form on Mars, with a mostly basaltic surface composition enriched in Fe compared  
335 the Earth's crust (Taylor and McLennan, 2008). More silica and iron are released during the  
336 early stages of aqueous alteration of mafic minerals (e.g., olivine and pyroxene) than felsic  
337 minerals (e.g., feldspars and quartz), and so hydrologic reservoirs (e.g., lakes, ground water) in  
338 basaltic terrains on Mars could readily be near silica and iron saturation levels (McLennan, 2003;  
339 Hurowitz et al., 2017; Tosca et al., 2018). A change in environmental conditions (pH, Eh,  
340 temperature) would control where and when iron and silica precipitate, and would also dictate  
341 the types of materials that form.

342 Iron solubility is more dependent on varying environmental conditions than silica.  
343 Circum-neutral to acidic (pH < 6-8) and reducing (low Eh) fluids can maintain relatively high  
344 Fe<sup>2+</sup> concentrations. If the pH of low-Eh Fe<sup>2+</sup>-bearing fluids increases, relatively insoluble Fe<sup>2+</sup>-  
345 hydroxides can precipitate, and if the Eh of Fe<sup>2+</sup>-bearing fluids increases, Fe<sup>3+</sup>-(hydr)oxide  
346 precipitation will occur at all pH > ~1-3, depending on overall composition (e.g., King and  
347 McSween, 2005). On the other hand, silica solubility increases steadily with increasing

348 temperature, and even more dramatically when pH reaches alkaline conditions (pH > ~9), so  
349 solutions could become significantly enriched in silica under alkaline conditions. In fact, basalt  
350 dissolution drives the pH of solutions toward more alkaline values (up to pH 10) due to proton  
351 consumption by mafic mineral constituents (e.g., Arnórsson et al., 2002). Periodic decreases in  
352 silica solubility could be caused by: a decrease in fluid pH through mixing with circum-neutral  
353 pH water, atmospheric CO<sub>2</sub>, or external acid sources; an increase in ionic strength with the  
354 concentration of ground waters (Siever, 1959); and/or temperature fluctuations. Any of these  
355 factors could cause silica to become supersaturated and force precipitation, and so fluid pH,  
356 temperature, or composition cannot be constrained by silica alone.

357         The FeO<sub>T</sub>-rich AmC material present in all Gale crater rocks does not necessarily  
358 represent a single composition precipitated by a single process, but likely represents  
359 compositionally variable assemblages consisting of several amorphous materials. Suboxic  
360 conditions might have formed Fe<sup>2+/3+</sup>-materials co-precipitated with silica, possibly green rust  
361 (Tosca et al., 2018). On the other hand, oxidizing conditions might have formed Fe<sup>3+</sup>-materials  
362 such as hisingerite (Fe<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub> · 2H<sub>2</sub>O) or silica + ferrihydrite (5Fe<sub>2</sub>O<sub>3</sub> · 9H<sub>2</sub>O) (Dehouck et  
363 al., 2014, 2017), similar to nanophase Fe<sup>3+</sup>-oxides detected in rocks and soils at Gusev crater and  
364 Meridiani Planum by the Mössbauer spectrometers onboard the *Spirit* and *Opportunity* rovers  
365 (Morris et al., 2006) and inferred in some Gale crater rocks from Mastcam spectra (Horgan et al.,  
366 2020). Poorly crystalline nontronite, Fe-sulfates (Sutter et al., 2017; Achilles et al., 2020),  
367 amorphous Fe-phosphate (Tu et al., 2014), anhydrous oxidative weathering products (Salvatore  
368 et al., 2013, 2019), and minor glass are also potential contributors to the FeO<sub>T</sub>-rich AmC  
369 material.

370         The estimated composition of the SiO<sub>2</sub>-rich AmC endmember is not pure silica, but could  
371 represent opaline silica intimately mixed with other phases, or cation-bearing X-ray amorphous  
372 silicates. Opaline silica forms in soils during pedogenesis (e.g., Chadwick et al., 1987; Drees et  
373 al., 1989), as chemical sediments on sea floors (e.g., Iijima and Tada, 1981), as precipitates from  
374 groundwater at springs and in sediments (e.g., Channing and Butler, 2007; Rodgers et al., 2003;  
375 Martin and Gaillou, 2018), and it is a cementing agent for many types of sedimentary rocks  
376 (Scholle and Ulmer-Scholle, 2003). In such natural environments, amorphous silica can co-  
377 precipitate with other materials. For instance, nanoparticles of amorphous iron and silica formed  
378 by chemical precipitation from the water column are thought to be the precursors for  
379 Precambrian banded iron formation rocks (e.g., Rasmussen et al., 2015). The “impurity” of the  
380 silica endmember could also be explained by (Mg<sup>2+</sup>, Fe<sup>2+/3+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>)-bearing X-ray  
381 amorphous silicates, such as those that have been shown to form during chemical weathering and  
382 alteration in cold climate mafic terrains (e.g., Rutledge et al., 2018; Thorpe et al., 2019; Smith et  
383 al., 2017). Amorphous silica-rich deposits have been detected across the Martian surface by both  
384 orbiter and rover-based instruments (e.g., Bandfield, 2002; Squyres et al., 2008; Milliken et al.,  
385 2008; Fraeman et al., 2016; Sun and Milliken, 2018; Tarnas et al., 2019), and in Martian  
386 meteorites using terrestrial laboratory techniques (e.g., Lee et al., 2015). The finding of an

387 amorphous silica-rich endmember throughout rocks drilled from Gale crater reinforces the  
388 importance of amorphous silica-forming processes throughout the history of the planet.

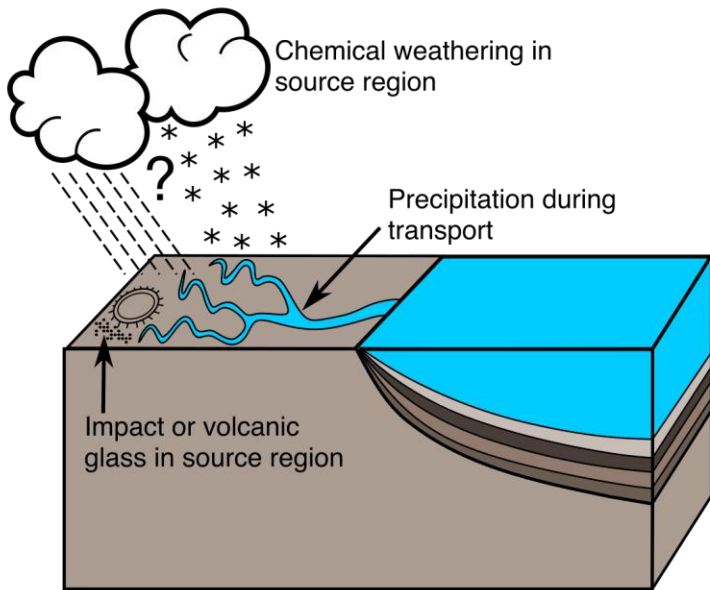
### 389 5.3 Constraining processes and timing in Gale crater

390 It is important to emphasize that AmC compositions could represent complex  
391 combinations of materials formed through different processes at different times. Sedimentary  
392 basins on Earth are reservoirs for detrital and authigenic sediments, with regional and local  
393 ground water circulation patterns and environmental conditions that vary significantly in space  
394 and time (e.g., Morad et al., 2000). All of these factors determine what phases are present at any  
395 given location or time. We see evidence for such variations within Gale crater as there are  
396 variable ratios of likely authigenic and/or diagenetic redox sensitive Fe-bearing minerals  
397 (magnetite and hematite), indicating variable Eh conditions within stratigraphic groups  
398 (Hurowitz et al., 2017; Rampe et al., 2020a and references therein). Additionally, later diagenetic  
399 fluids could overprint detrital or earlier diagenetic deposits.

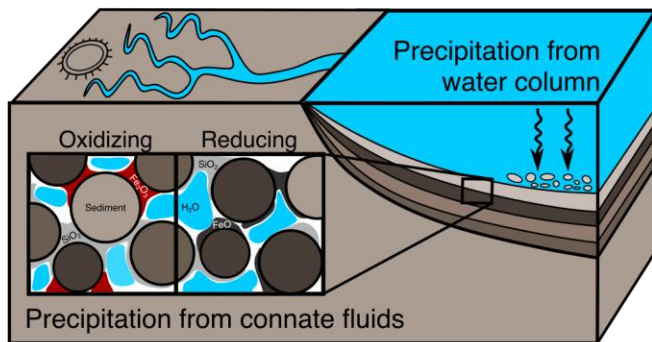
400 We separate possible formation processes for Gale crater amorphous  $\text{SiO}_2$ - and  $\text{FeO}_T$ -  
401 bearing materials into three time frames: (1) pre-deposition of sediments (i.e., provenance and  
402 chemical weathering history in the sediment source region), (2) syn-deposition to early post-  
403 deposition of sediments (i.e., authigenic to early diagenetic), and (3) post-deposition of  
404 sediments (i.e., mid to late diagenetic) (Figure 4). X-ray amorphous materials formed in the pre-  
405 deposition time frame would have formed in the source region before being transported to the  
406 crater (i.e., detrital; Figure 4, top). As such, these materials would indicate processes happening  
407 in the source regions around the late Noachian epoch (Thomson et al., 2011), a time period over  
408 which there is continuing debate about if the climate was warm and wet, cold and icy, or  
409 somewhat variable at any given time (e.g., Wordsworth, 2016; Ramirez and Craddock, 2018;  
410 McLennan et al., 2019). Authigenic amorphous materials formed during the syn-depositional to  
411 early post-depositional time frame would be indicative of physicochemical conditions in the  
412 lakes and sediment pore spaces (connate fluids) around the time of deposition (Figure 4, middle).  
413 Precipitation of chemical precipitates from the water column would allow for chemical  
414 sediments to build up along with the detrital siliciclastic sediments (syndepositional). Shortly  
415 following deposition on the crater floor, and with increased burial, water trapped in the sediment  
416 pore spaces might precipitate cements (e.g., Siever, 1959; Pettijohn et al., 1987). Post-  
417 lithification (i.e., mid to late diagenesis), authigenic X-ray amorphous materials could also have  
418 formed from interactions with locally or regionally sourced diagenetic fluids circulating through  
419 the rocks (Figure 4, bottom). This later time period is typically characterized by much more  
420 extensive cementation during moderate burial (mid diagenesis; e.g., Siever, 1959; Pettijohn et al.,  
421 1987), and alteration reactions (late diagenesis; e.g., Morad et al., 2000).

422

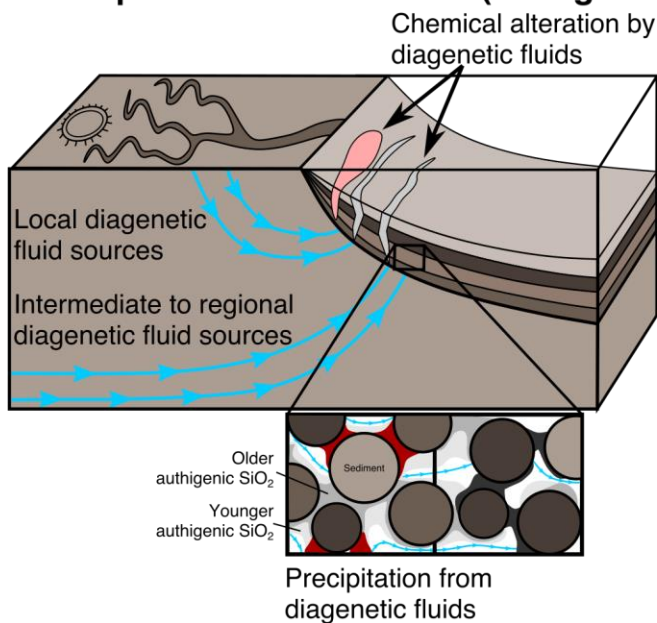
### Pre-deposition of sediments (detrital)



### Syn-depositional to early diagenesis (authigenic)



### Post-deposition of sediments (authigenic)



424 **Figure 4.** Illustrations showing the relative timing of the potential processes forming the  
425 amorphous SiO<sub>2</sub> and FeO<sub>T</sub> components of sedimentary rocks in Gale crater. (**Top**) Detrital  
426 amorphous materials could have formed through volcanic eruptions or impacts (glass), chemical  
427 weathering in the source region, or during fluvial transport before being deposited in Gale crater.  
428 (**Middle**) Authigenic amorphous materials could have formed during sediment deposition by  
429 precipitation from the water column as chemical sediments or from connate fluids as pore space  
430 cement after sediment deposition. (**Bottom**) Authigenic amorphous materials could have formed  
431 after sediment deposition by precipitation from diagenetic fluids in remaining pore spaces or by  
432 chemical alteration of the lithified rock with diagenetic fluids.

433 Crosscutting relationships and geologic context provide evidence that some of the AmCs  
434 are related to late diagenetic processes. Two of the most SiO<sub>2</sub>-rich AmCs are found in alteration  
435 halos (GH and LB) associated with fractures that crosscut the Siccar Point group parent rocks,  
436 indicating that the alteration took place sometime after the rocks were lithified and fractured  
437 (Frydenvang et al., 2017; Yen et al., 2017; Hausrath et al., 2018). This crosscutting relationship  
438 also indicates that the compositionally distinct AmCs in the parent rocks were formed earlier  
439 (pre-deposition to mid diagenesis time frames).

440 Late diagenetic AmC SiO<sub>2</sub>-enrichment may not have been limited to the Siccar Point  
441 group rocks. Gabriel et al. (2019) reported on a large fracture network in the Bradbury group that  
442 shows similar surface expression, geochemical trends, and estimated water content compared to  
443 the fracture-associated halos in the Siccar Point group. Additionally, while not associated with  
444 fractures, the Buckskin (BK), Oudam (OU), Stoer (ST), and Highfield (HF) drill hole locations  
445 in the Mount Sharp group have AmCs that are very enriched in SiO<sub>2</sub> compared to the drill hole  
446 locations stratigraphically above and below, suggesting localized fluid interactions (e.g., Morris  
447 et al., 2016; Achilles et al., 2020; Yen et al., 2020). Fluids migrating through localized zones in  
448 the rocks could have either provided a new silica source (e.g., Frydenvang et al., 2017) or  
449 allowed for the passive enrichment of silica by leaching (e.g., Yen et al., 2017) or by  
450 crystallizing amorphous iron oxides (e.g., Achilles et al., 2020; discussed below). Accordingly,  
451 the most SiO<sub>2</sub>-rich AmCs observed in Gale crater thus far may result from fluid interactions long  
452 after the lithification of the parent sedimentary rocks. The fact that these observations occur  
453 across the rover traverse suggest that localized fluids were widespread throughout Gale crater,  
454 possibly over long periods of time, at least until after the youngest sedimentary rocks had been  
455 lithified.

456 Not all amorphous SiO<sub>2</sub> enrichment resulted from localized late diagenetic fluids. The  
457 broad increase in AmC abundance and SiO<sub>2</sub> content across the Bradbury – Mount Sharp  
458 boundary coincides with differences in provenance (Siebach et al., 2017; Bedford et al., 2018)  
459 and an observed increase in bulk rock SiO<sub>2</sub> (Hurowitz et al., 2017). Hurowitz et al. (2017)  
460 hypothesized that increased bulk rock SiO<sub>2</sub> was evidence for amplified source region chemical  
461 weathering due to wetter climate conditions during deposition of the Mount Sharp group, and  
462 bulk rock chemical analyses provide further evidence that Mount Sharp group rocks are more  
463 intensely weathered (e.g., Siebach et al., 2017; Mangold et al., 2019). Increased weathering  
464 could have supplied detrital X-ray amorphous (Mg<sup>2+</sup>, Fe<sup>2+/3+</sup>)-rich silicates along with the  
465 crystalline detrital sediments (Figure 4, top), and SiO<sub>2</sub>-bearing, alkaline surface- and ground-  
466 waters to Gale crater (Figure 4, middle and bottom). Decreases in pH by mixing with circum-  
467 neutral waters, or even local evaporation could have allowed for silica supersaturation, possibly



468 leading to precipitation from the water column or in pore spaces as cements. Thus, the overall  
469 enrichment in amorphous silica for the Mount Sharp group rocks, relative to the Bradbury group  
470 rocks, is likely due to processes in the pre-depositional through mid-diagenesis time frames, with  
471 additional amorphous silica enrichment in some locations resulting from late diagenetic  
472 overprinting (BK, OU, ST, and HF, as discussed above).

#### 473 5.4 The problem with preservation

474 It is not necessarily difficult to form X-ray amorphous materials on Mars, and in theory it  
475 would not be difficult to accumulate them in a sedimentary basin such as Gale crater, a terminal  
476 sink for materials formed through a variety of processes. But their preservation for up to billions  
477 of years is a major conundrum for understanding the Martian sedimentary rock cycle (McLennan  
478 et al., 2019). X-ray amorphous materials are metastable and are thought to recrystallize on very  
479 short timescales (e.g., Curtis, 1977, 1990; Siever, 1983; Tosca and Knoll, 2009). Crystallization  
480 processes such as Ostwald ripening (Steeffel and Van Cappellen, 1990) and crystallization  
481 through particle attachment (De Yoreo et al., 2015) result from prolonged aqueous interactions  
482 which drive dissolution/precipitation processes that allow atomic and particle rearrangements  
483 to take place. Thus, more crystalline alteration products are formed at the expense of amorphous  
484 materials through particle coarsening processes determined by both kinetic and thermodynamic  
485 factors. As a result, X-ray amorphous materials have yet to be found in significant abundances in  
486 rocks of comparable age (> 1 Gy) on Earth. Indeed, on Earth X-ray amorphous materials of  
487 greater than ~10 My in age are exceedingly rare in sedimentary rocks.

488 Based on the crystalline mineralogy at each drill hole location, there is some indication  
489 that portions of the AmC materials might have been converted to more crystalline materials  
490 during diagenesis. For instance, opal-CT is detected in the Oudam (OU) drill hole sample, which  
491 may represent the diagenesis of opal-A (Achilles et al., 2020). Another example is the Stoer (ST)  
492 drill hole sample, which has an anomalous AmC composition compared to other drill hole  
493 locations with moderate AmC abundances. The FeO<sub>T</sub>-poor, SiO<sub>2</sub>-rich AmC of Stoer coupled  
494 with the highest hematite abundances detected at VRR (Rampe et al., 2020b) could be evidence  
495 for the crystallization of hematite from originally amorphous FeO<sub>T</sub> during diagenetic fluid  
496 interactions. Despite the fact that some fraction of the AmC materials might have been converted  
497 to more crystalline alteration products, all of these sedimentary rocks contain significant  
498 abundances of X-ray amorphous materials that have been preserved for billions of years.

499 Orbital detections of hydrated amorphous silica (and other poorly crystalline minerals) in  
500 ancient deposits across the Martian surface led Tosca and Knoll (2009) to conclude that the  
501 preservation of such phases indicated a water-limited environment since they formed. However,  
502 our understanding of Martian aqueous history has changed significantly with the study of Gale  
503 crater by the *Curiosity* rover (see review in McLennan et al., 2019). Along with the results from  
504 this study, there is substantial evidence for a long history of water-rock interactions in Gale  
505 crater (e.g., Léveillé et al., 2014; Stack et al., 2014; Nachon et al., 2014, 2017; Frydenvang et al.,  
506 2017; Kah et al., 2018; Minitti et al., 2019; Sun et al., 2019). In fact, likely diagenetic jarosite in  
507 the Mount Sharp group sample MJ has a K-Ar age date <3 Ga and possibly as young as ~2.1 Ga,  
508 showing that diagenetic fluids circulated through the buried sediments for up to a billion years or  
509 more post emplacement (Martin et al., 2017). A long history of liquid water in Gale crater,  
510 however, does not necessarily mean that liquid water was continuously present for billions of

511 years. Perhaps shorter durations of water-rock interactions might have allowed amorphous  
512 materials to form but not transform to crystalline products. Nevertheless, given our current  
513 knowledge about the instability of X-ray amorphous materials, it continues to remain unclear  
514 how the X-ray amorphous materials in Gale crater have been preserved nearly intact through to  
515 the present-day.

## 516 **6 Conclusions and Outstanding Questions**

517 AmC SiO<sub>2</sub> and FeO<sub>T</sub> contents are anti-correlated suggesting a mixing relationship  
518 between hypothetical SiO<sub>2</sub>-rich and FeO<sub>T</sub>-rich AmC endmembers. The compositions of the  
519 hypothetical endmembers are inconsistent with volcanic or impact glass alone, and so we  
520 conclude that the SiO<sub>2</sub> and FeO<sub>T</sub> contents in the X-ray amorphous material in Gale crater  
521 sedimentary rocks formed largely through aqueous processes.

522 The individual constituents of the AmCs likely formed through aqueous processes  
523 occurring both outside and inside the crater at different times, such that the bulk AmCs represent  
524 mixtures of individual X-ray amorphous materials (e.g., weathering products, chemical  
525 sediments, and diagenetic cements) accumulated over time. The FeO<sub>T</sub>-rich AmC materials likely  
526 comprise mixtures of Fe-silicates, ferrous or ferric oxide nanoparticles, SiO<sub>2</sub>, Fe-sulfates, various  
527 non-Fe-bearing amorphous materials, and minor glass. The hypothetical SiO<sub>2</sub>-rich endmember is  
528 not pure opaline silica, but could represent opaline silica co-precipitated with other phases (e.g.,  
529 sulfates) or cation-rich silicates.

530 The AmC SiO<sub>2</sub> and FeO<sub>T</sub> contents in Gale crater rocks represent materials mostly formed  
531 through long-lived aqueous processes that started before the first sediments were deposited in the  
532 crater (late Noachian), and did not end until well after the youngest sediments were lithified (mid  
533 Hesperian, possibly late Hesperian). Cross-cutting relationships and geologic context provide  
534 evidence that the most SiO<sub>2</sub>-rich AmCs observed in Gale crater thus far may result from  
535 localized fluids having either provided a new silica source or passively enriched the rocks in  
536 silica long after the lithification of the parent sedimentary rocks. On the other hand, AmCs with  
537 moderate to low SiO<sub>2</sub> contents likely formed much earlier in the pre-depositional through mid  
538 diagenetic time frames.

539 Two fundamental problems remain in understanding the amorphous components of  
540 Martian sedimentary rocks. The first is why is there so much amorphous material of such  
541 variable composition in Martian sedimentary rocks, and the second is how are these materials  
542 preserved over billions of years? Perhaps at a fundamental level these questions are related. The  
543 basic mechanisms identified for the formation of possible amorphous components in Martian  
544 sedimentary rocks are individually well-documented and well-understood from the terrestrial  
545 sedimentary rock record: igneous and impact glasses, chemical weathering products, chemical  
546 sedimentation, precipitation of syn-depositional through late stage diagenetic phases (e.g., Curtis,  
547 1977; Pettijohn et al., 1987). However, on Earth, these phases are thermodynamically unstable  
548 and recrystallize on very short timescales (e.g., Curtis, 1977, 1990; Siever, 1983; Tosca and  
549 Knoll, 2009; also see De Yoreo et al., 2015). Accordingly, amorphous materials formed by  
550 different processes are less likely to accumulate throughout the source-to-sink history of a  
551 sedimentary rock, and where they are more likely to accumulate (e.g., chemical and fine-grained  
552 clastic sedimentary rocks) they do not persist long after burial (Curtis, 1990). On Mars, the

553 situation appears to be different in that there must be long-lived ( $>10^9$  yr), but poorly understood,  
554 kinetic, or perhaps even thermodynamic (e.g., persistent metastability; De Yoreo et al., 2015),  
555 impediments to the recrystallization of amorphous materials. In addition, the basaltic nature of  
556 the eroding Martian crust is likely to be more efficient in forming amorphous materials,  
557 especially during early stages of chemical weathering, than is the granitic upper continental crust  
558 of the Earth (e.g., McLennan, 2003). Thus, for Martian sedimentary rocks, perhaps it should not  
559 be unexpected that amorphous materials, derived from a variety of sources and processes,  
560 accumulate in sedimentary rocks throughout the source-to-sink history and diagenesis. Such a  
561 history would lead to both relatively high abundances of amorphous materials and to a diversity  
562 of amorphous phases compared to what is typically seen in the terrestrial sedimentary record.  
563 Nevertheless, although post-depositional aqueous history is likely to be a factor, the reasons for  
564 the exceptional persistence of such materials in the Martian geological record remains largely an  
565 open question.

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567 There are no real or perceived financial conflicts of interests for any author. All data  
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