Silicic volcanism on Mars evidenced by tridymite in high-SiO₂ sedimentary rock at Gale crater


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The Mars Science Laboratory (MSL) rover, Curiosity, has been exploring sedimentary rocks within Gale crater since landing in August 2012, and progressing upward through a sequence of strata exposed along the lower slopes of Aeolis Mons (informally known as Mount Sharp). This traverse has taken Curiosity through sequences of effusive, deltaic, and lacustrine sediments (e.g., ref. 1). On sol 1057 (the number of martian days since landing), Curiosity began preparations for collecting drill powder from high-silica sedimentary rock at a location named Buckskin. We describe the geochemical setting of the Buckskin sample location, the detection of significant amounts of the silica polymorph tridymite by the MSL Chemistry and Mineralogy (CheMin) X-ray diffraction instrument, and its implications for volcanism on Mars.

**Geologic Setting**

The Buckskin outcrop is part of the Murray formation of lacustrine mudstones exposed in the Marias Pass area (SI Appendix, Figs. S1 and S2). The formation was previously studied in the Pahrump Hills (1), where three drill samples were analyzed by CheMin [Confidence Hills, Mojave2, and Telegraph Peak (2)]. With the assumption that bedding is approximately horizontal, the Marias Pass outcrop is ~2–3 m thick and ~6 m higher in stratigraphic position than the highest outcrop sampled in the Pahrump Hills (Telegraph Peak (1)). Mudstone, generally characterized by fine laminae, is the dominant depositional facies in the Pahrump Hills (1) and also at Marias Pass, as shown by the Mars Hand Lens Imager images of Marias Pass bedrock and the dust-free float rock Lamoosge (Fig. 14). Here the laminae have a mean thickness of ~0.5 mm and are characteristically parallel; individual laminae are laterally continuous for at least several tens of centimeters. The mudstone facies lacks evidence for cross-stratification at any scale, sediment

Mars | tridymite | Gale crater | lake | volcanism

Tridymite, a low-pressure, high-temperature (>870 °C) SiO₂ polymorph, was detected in a drill sample of laminated mudstone (Buckskin) at Marias Pass in Gale crater, Mars, by the Chemistry and Mineralogy X-ray diffraction instrument onboard the Mars Science Laboratory rover Curiosity. The tridymite mudstone has ~40 wt.% crystalline and ~60 wt.% X-ray amorphous material and a bulk composition with ~74 wt.% SiO₂ (Alpha Particle X-Ray Spectrometer analysis). Plagioclase (~17 wt.% of bulk sample), tridymite (~14 wt.%), sanidine (~3 wt.%), cation-deficient magnetite (~3 wt.%), cristobalite (~2 wt.%), and anhydrite (~1 wt.%) are the mudstone crystalline minerals. Amorphous material is silica-rich (~39 wt.% opal-A and/or high-SiO₂ glass and opal-CT), volatile-bearing (16 wt.% mixed cation sulfates, phosphates, and chlorides- perchlorates–chlorates), and has minor TiO₂ and Fe₂O₃-T oxides (~5 wt.%). Rietveld refinement yielded a monoclinic structural model for a well-crystalline tridymite, consistent with high formation temperatures. Terrestrial tridymite is commonly associated with silicic volcanism, and detritus from such volcanism in a “Lake Gale” catchment environment can account for Buckskin’s tridymite, cristobalite, feldspar, and any residual high-SiO₂ glass. These cogenetic detrital phases are possibly sourced from the Gale crater wall/rim/central peak. Opaline silica could form during diagene-sis from high-SiO₂ glass, as amorphous precipitated silica, or as a residue of acidic leaching in the sediment source region or at Maris Pass. The amorphous mixed-cation salts and oxides and possibly the crystalline magnetite (otherwise detrital) are primary precipitates and/ or their diagenesis products derived from multiple infiltrations of aqueous solutions having variable compositions, temperatures, and acidities. Anhydrite is post lithification fracture/vein fill.

Significance

Tridymite, a SiO₂ mineral that crystallizes at low pressures and high temperatures (>870 °C) from high-SiO₂ materials, was detected at high concentrations in a sedimentary mudstone in Gale crater, Mars. Mineralogy and abundance were determined by X-ray diffraction using the Chemistry and Mineralogy instrument on the Mars Science Laboratory rover Curiosity. Terrestrial tridymite is commonly associated with silicic volcanism where high temperatures and high-silica magmas prevail, so this occurrence is the first in situ mineralogical evidence for martian silicic volcanism. Multistep processes, including high-temperature alteration of silica-rich residues of acid sulfate leaching, are alternate formation pathways for martian tridymite but are less likely. The unexpected discovery of tridymite is further evidence of the complexity of igneous petrogenesis on Mars, with igneous evolution to high-SiO₂ compositions.


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Data deposition: CheMin and APXS experiment data records and CheMin diffraction patterns have been deposited with the NASA Planetary Data System at pubs.geosciences. wustl.edu/education/msl-i-mesh-chem-4-vr/1mmslon1__1xxx for the CheMin data and pubs.geosciences. wustl.edu/education/msl-i-apxs-4_s-1dvlhmslaps_1xxx for the APXS data.

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transport (or erosion) by traction currents, sediment-filled mud-cracks, intraclasts that indicate reworking of mud by currents, or clasts. The observed features are characteristic of lacustrine sedimentation and contrast strongly with subaerial settings associated with eolian, fluvial, volcanic, or impact processes (1).

### Buckskin Mineralogical Composition

Targets for chemical analyses by the Alpha Particle X-Ray Spectrometer (APXS) at the Buckskin site included tailings from the test drill hole (sol 1059), the sample acquisition hole (sol 1064; Fig. 1A), and dump piles from emptying the Collection and Handling for In-Situ Martian Rock Analysis tool before (sol 1065) and after (sol 1091) the collected drill powder was sieved to <150 μm [see MSL mission overview for background (3)]. The chemical similarity of APXS analyses of the presieve and postsieve dump piles (Table 1) indicates that mineralogical fractionation between bulk sample and CheMin-analyzed sample (<150-μm postsieve dump pile) is minimal.

CheMin is a transmission X-ray diffraction (XRD) and X-ray fluorescence instrument that uses cobalt radiation to produce two-dimensional Co Kα diffraction images (Debye ring pattern) (4). Samples are normally measured over the course of three nights, producing 45 total images that are summed and converted to a one-dimensional diffraction pattern over an angular range of 2–52° 2θ. The diffraction pattern used for Buckskin quantitative XRD analysis was the sum of the first 4 of 45 diffraction images, and tridymite peaks are clearly evident (Fig. 2). The remaining 41 images are affected by on-ring and off-ring diffraction spots. Coincident with the appearance of abundant spots are a decrease in the intensities of tridymite diffraction peaks (by ∼50%) and a concomitant increase in the intensities of anhydrite diffraction peaks. This observation is based on a comparison of diffraction patterns for the sum of images 1 through 4 and 16 through 45, with each normalized to 45 images (i.e., the same integration time) (SI Appendix, Fig. S3). The explanation for the change in the nature of the diffraction patterns after image 4, possibly resulting from poor grain motion and particle clumping, is under investigation.

For quantitative analysis of CheMin XRD data, we used the full pattern-fitting capability (Rietveld) in Jade (Materials Data Inc.), with refinement of literature cell parameters (5) for well-crystalline minerals present at >5 wt.% abundance, and FULLPAT analysis for poorly crystalline and XRD-amorphous phases (6–9). The combined results from both analyses are listed in Table 2. Unit cell parameters were refined for tridymite, plagioclase, sanidine, and magnetite (Table 3). The two most abundant crystalline minerals are plagioclase (43 wt.% of crystalline material; ∼4Al4Si5) and tridymite (34 wt.%). All tridymite principal diffraction intensities (10) are present and well defined at instrument resolution (Table 4 and Fig. 2). They are indicative of fully ordered monoclinc tridymite, originally formed at high temperatures, as opposed to a disordered material like opal-CT, which has broad diffraction peaks that represent portions of a disordered tridymite structure in the 4.05–4.10 Å and 2.50 Å regions and with a weak diffraction peak at 4.25–4.35 Å (11). There are suggestions in the literature that opal-T can exist as a substance more ordered toward tridymite than opal-CT, which would be recognized by a broad diffraction peak near 4.107 Å and weaker broad diffraction peaks near 4.326 Å and 2.50 Å (12). However, the Buckskin tridymite shows none of these characteristics. Refined diffraction patterns for plagioclase, tridymite, sanidine, and magnetite are illustrated in SI Appendix, Fig. S4, as well as patterns of cristobalite and anhydrite whose unit cell parameters were fixed during refinement.

The poorly crystalline or XRD-amorphous material was modeled by contributions from opal-A, obsidian, and opal-CT to account for the diffuse diffraction feature centered near 26° 2θ and a low-angle scattering component that also includes a diffuse ferrhydrite-like diffraction feature centered near 40° 2θ (SI Appendix, Fig. S5). Instrumental artifacts, including a peak near 6.6° 2θ (∼15 Å) from the Kapton cell window, were modeled using CheMin patterns from analyses of empty cells with Kapton windows. Although opal-A was used to model the amorphous material, any high-SiO2 phase with a similar XRD pattern can be used, including SiO2 glass, gem opal, and silica gel. (See SI Appendix, Fig. S6 for XRD patterns of amorphous high-SiO2 materials produced by synthetic and natural

### Table 1. Composition of presieve and postsieve dump piles (from APXS) and calculated compositions of crystalline and amorphous materials

<table>
<thead>
<tr>
<th></th>
<th>Presieve, wt.%</th>
<th>Postsieve, wt.%</th>
<th>Crystalline, wt.%</th>
<th>Amorphous, wt.%</th>
</tr>
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<tr>
<td>SiO2</td>
<td>74.43</td>
<td>73.65</td>
<td>68.20</td>
<td>77.01</td>
</tr>
<tr>
<td>TiO2</td>
<td>1.66</td>
<td>1.57</td>
<td>0.12</td>
<td>2.54</td>
</tr>
<tr>
<td>Al2O3</td>
<td>5.45</td>
<td>5.66</td>
<td>13.91</td>
<td>0.04</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>0.08</td>
<td>0.10</td>
<td>0.00</td>
<td>0.17</td>
</tr>
<tr>
<td>FeOT</td>
<td>4.94</td>
<td>5.49</td>
<td>7.27</td>
<td>4.71</td>
</tr>
<tr>
<td>MnO</td>
<td>0.08</td>
<td>0.09</td>
<td>0.00</td>
<td>0.15</td>
</tr>
<tr>
<td>MgO</td>
<td>0.72</td>
<td>0.82</td>
<td>0.16</td>
<td>1.26</td>
</tr>
<tr>
<td>CaO</td>
<td>2.99</td>
<td>3.05</td>
<td>5.25</td>
<td>1.54</td>
</tr>
<tr>
<td>Na2O</td>
<td>2.01</td>
<td>2.08</td>
<td>2.80</td>
<td>1.58</td>
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<tr>
<td>K2O</td>
<td>0.99</td>
<td>0.96</td>
<td>1.35</td>
<td>0.69</td>
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<tr>
<td>P2O5</td>
<td>1.29</td>
<td>1.25</td>
<td>0.00</td>
<td>2.09</td>
</tr>
<tr>
<td>SO3</td>
<td>4.85</td>
<td>4.80</td>
<td>1.06</td>
<td>7.31</td>
</tr>
<tr>
<td>Cl</td>
<td>0.28</td>
<td>0.29</td>
<td>0.00</td>
<td>0.49</td>
</tr>
<tr>
<td>Total</td>
<td>99.77</td>
<td>99.81</td>
<td>100.12</td>
<td>99.60</td>
</tr>
</tbody>
</table>

*Amorphous material composition calculated using APXS postsieve dump pile analysis as bulk composition, 40 wt.% crystalline material, and 60 wt.% amorphous material.
Fig. 2. Buckskin diffraction pattern (red) from sum of first four diffraction 
images, calculated pattern from Rietveld analysis (black), difference pattern 
(blue), and refined tridymite pattern (offset green); see SI Appendix, Fig. S4 for 
refined patterns of all minerals. Full width at half maximum intensity (FWHM) 
of the tridymite peak at 2θ=23.9° 2θ is 0.27° 2θ, which corresponds to CheMin 2θ/ 
resolution measured on Earth before launch (ref. 4, figure 18). Peak at ~6.5° 2θ 
is from the Kapton cell window.

processes.) The amount of amorphous material in the bulk sample 
based on FULLPAT is 50 ± 15 wt.% (Table 2).

Chemistry of Crystalline and Amorphous Materials

The chemical compositions of Buckskin plagioclase, tridymite, sanidine, and magnetite were estimated from unit cell parameters 
calculated by Rietveld refinement (Table 3). However, mineral unit 
cell parameters are insensitive to abundances of trace and minor 
elements (e.g., Fe in plagioclase). To limit artificial assignments of 
these elements to the amorphous material, we adopted composi-
tions of naturally occurring materials for the chemical compositions 
of plagioclase, tridymite, and sanidine (13-15), subject to the 
constraint that their compositions are consistent with those derived 
from XRD unit cell parameters (Table 3 and SI Appendix, Table S1). This approach was more difficult for magnetite, because its 
refined cell (a = 8.359 ± 0.001 Å; Table 3) is too small for sto-
ichiometric magnetite [Fe₃O₄; a = 8.394 Å (5)]. The cell parameters 
and bulk rock composition are most consistent with cation-deficient 
magnetite (Fe₂₋iplesO₄) to accommodate the observed magnetite 
unit cell parameters. Alternatives to reduce the magnetite unit 
cell parameters that are not reasonable based on the mineral composi-
tion of the rock (Table 1) include a chromite [Fe³⁺(Cr, Fe³⁺)₂O₄] 
component (too little Cr) and hercynite (FeAl₂O₄) or spinel 
(MgAl₂O₄) components (all Al is associated with feldspar). An 
ulvöspinel (Fe₂TiO₄) component gives a larger cell parameter 
and is thus metastable under ambient terrestrial (and martian) 
surface conditions. It is readily produced under laboratory condi-
tions within its stability field, especially with alkali fluxes (18-27).

Tridymite Formation Pathways

Tridymite is the stable polymorph of SiO₂ at low pressures (up to 
~0.4 GPa) between ~870 °C and ~1,470 °C (e.g., refs. 16 and 17) 
and is thus metastable under ambient terrestrial (and martian) 
surface conditions. It is readily produced under laboratory condi-
tions within its stability field, especially with alkali fluxes (18-27).

Table 2. Mineralogy of Buckskin drill sample relative to 
crystalline material and relative to bulk sample using XRD-
and APXS-derived concentrations for the amorphous material

<table>
<thead>
<tr>
<th>Mineral</th>
<th>XRD*</th>
<th>APXS*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plagioclase</td>
<td>21.4 ± 1.5</td>
<td>17.1 ± 1.2</td>
</tr>
<tr>
<td>Sanidine</td>
<td>4.2 ± 0.9</td>
<td>3.4 ± 0.7</td>
</tr>
<tr>
<td>Magnetite</td>
<td>3.4 ± 0.4</td>
<td>2.8 ± 0.3</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>0.9 ± 0.3</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>Tridymite</td>
<td>17.1 ± 1.0</td>
<td>13.6 ± 0.8</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>3.0 ± 0.4</td>
<td>2.4 ± 0.3</td>
</tr>
<tr>
<td>Amorphous</td>
<td>50 ± 15*</td>
<td>60^{+4}_{-3}</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

*Units = wt.%; uncertainties are 2σ.
†Includes contributions from the broad hump centered near 2θ = 20° (modeled 
as opa-A plus obudian (33 wt.% of bulk sample) and opa-CT (6 wt.%) and 
the broad hump centered near 40° 2θ modeled as ferricydrude plus low-angle 
scattering (21 wt.%) (SI Appendix, Fig. S5).
‡Lower limit; constrained by APXS chemistry.
Acid sulfate leaching of rhyolite also occurred there, increasing the SiO$_2$ concentration from $\sim$71 wt.% to $\sim$97 wt.%.

The temperature regime associated with basaltic and intermediate volcanism can also provide a formation pathway for tridymite when the requisite high-SiO$_2$ material is present. Pyroclastic flows and associated ash plumes generated by partial lava dome collapse at andesitic Soufriere Hills volcano (Montserrat) have 10–27 wt.% tridymite plus cristobalite with minor quartz in their <10-μm size fraction (41). The tridymite and cristobalite are inferred to have formed via vapor-phase crystallization and devitrification of rhyolitic glass (~78 wt.% SiO$_2$) within the lava dome. In altered basalts from Stromboli volcano (Aeolian Islands, Italy) and andesites from Augustine volcano (Alaska), the high-SiO$_2$ host for tridymite is the residue after acid sulfate leaching of primary mafic rock (42, 43). Pyrometamorphic ejecta (buddite) blocks (tridymite–clinopyroxene facies) have up to ~90 vol.% tridymite at Stromboli volcano. Occurrences of quartz paramorphs after tridymite have been reported in contact metamorphic assemblages between high-SiO$_2$ rocks and basaltic lava (e.g., refs. 44–46); however, quartz and not tridymite would be detected by CheMin for an equivalent assemblage at Gale crater. The high concentrations of tridymite (~14 wt.% of bulk sample) and SiO$_2$ (~74 wt.%) for the Buckskin sample are not reasonably sourced from low-silica volcanics for which tridymite concentrations would be very low when averaged over the volumetric equivalent of a “Lake Gale” catchment involving entirely basaltic to intermediate volcanics.

Tridymite has been reported at terrestrial impact structures where target lithologies are SiO$_2$-rich and heated to elevated temperatures by the impact event (47, 48). Monocrystalline tridymite was reported (abundance not quantified) in a core from the Chesapeake Bay impact structure, but only in a silica-rich 5-εm interval (~70 wt.% SiO$_2$ relative to whole rock) (48). In cores from the Popigai impact structure (gneiss target lithology), we calculate from ref. 47 that the mean tridymite concentration of melt rocks is ~1 vol.%, although up to ~5 vol.% tridymite is reported for several individual melt rocks. The impact that created Gale crater (~150 km diameter) generated a melt pool possibly of 0.5–1 km thickness (49) and presumably injected impact melt into fractured crater walls and central uplift. Even if the preimpact target lithology were SiO$_2$-rich (an assumption implying silicic volcanism predating the Gale impact), the high tridymite concentration in the Buckskin laminated mudstones is unlikely sourced from a Lake Gale catchment of impact melt rocks given the low tridymite abundance of known impactites.

As with terrestrial occurrences, tridymite in extraterrestrial samples has also been inferred to result from high-temperature igneous and/or impact processes on parent bodies or to form by direct condensation at high temperatures in the solar nebulae (e.g., refs. 24 and 50–58). Tridymite, cristobalite, quartz, and/or silica-rich glass are reported as minor constituents of lunar samples (e.g., ref. 57) and martian meteorites (e.g., refs. 51, 53, and 59). A granitic microcrast in polymict ureilite EET 87720 contains a phase tentatively identified as tridymite by micro-XRD, with ~98 wt.% SiO$_2$ (58). The bulk composition of the microclast (excluding interstitial glass) has ~77 wt.% SiO$_2$, and the interstitial glass is silica-rich (SiO$_2$ ~73 wt.%) and volatile-rich (~11 wt.% SO$_3$ and ~1 wt.% Cl). According to ref. 58, this microclast is evidence for an evolved melt on an unknown parent body with isotopic and volatile element data possibly pointing to Mars.

Tridymite has been synthesized in the laboratory by heating amorphous SiO$_2$ at 196 °C in glycol solutions (60). Aside from the fact that the chemical composition of the solutions used in these experiments is not geologically realistic, the temperature of the experiments is higher than those inferred so far for diagenesis at Gale crater (<~80 °C (8)), and the relative intensities of the diffraction peaks for the tridymite synthesized by ref. 60 differ markedly from those for the well-crystalline Buckskin tridymite (Table 4). These experiments indicate that low-temperature synthesis of metastable tridymite is possible and should be further explored. The apparent absence in nature of tridymite formation at low temperatures, based on studies of terrestrial and extraterrestrial rocks over many years (61–72) (see SI Appendix), suggests that this is an unlikely explanation for the large quantities of tridymite observed in the Buckskin sample.

**Significance of Tridymite in the Murray Formation**

In the absence of a geologically credible, low-temperature formation pathway for tridymite, and based on the consistency of its occurrences in natural samples as discussed in *Tridymite Formation Pathways*, we infer that tridymite in the Murray formation (Buckskin drill sample)
is a marker for low-pressure and high-temperature (≥870 °C) processes, consistent with its stability field, and high-SiO₂ precursor lithologies. Silicic volcanism fits the geologic, thermal, and mineralogical context best, with tridymite being incorporated into the Murray formation laminated mudstone (i.e., tridymitic mudstone) at Buckskin as detrital sediment from erosion of silicic volcanic rocks. It follows that, if cogenetic, the cristobalite, sanidine, plagioclase, and any amorphous high-SiO₂ glass are also detrital. The high-SiO₂ glass would constitute some unknown fraction of the amorphous silica material determined by CheMin (33 wt. % of bulk as opal-A and/or high-SiO₂ glass). However, we infer, from the presence of opal-CT in the Buckskin amorphous material, that any glass has undergone diagenesis at least in part if not wholly to opal-A and opal-CT. This diagenesis could have occurred in the volcanic source area or subsequent to lithification of tridymitic mudstone at Marias Pass. If the diagenesis took place in the source region, the opaline material is detrital.

Lacustrine sediments in cores from Lake Tecocomulco (Mexico), with a catchment basin that includes basaltic–andesitic, andesitic, and rhyolitic volcanic rocks (73), provide an appropriate terrestrial analog to an ancient Lake Gale and the Murray formation. Sedimentary units in core T-A95 from that lake include both fine-grained elastic sediments and coarser-grained dacite–rhyolite air-fall tephra. The highest combined abundance of tridymite plus cristobalite (up to >30% with no quartz) are in unit IIIa, a silty sand clastic sediment with ~60 wt. % SiO₂. Tridymite and cristobalite are present at generally lower abundances (5–30%) in two air-fall tephra layers in unit IIIb (~70 wt. % SiO₂) from Plinian eruptions 8–60 km away (73). The Lake Tecocomulco analog shows that sediments with high abundances of tridymite and cristobalite, like those in the Buckskin sample, are obtainable in lake sediments with a catchment that includes silicic volcanism.

By partial analogy with tridymite-bearing sediments in Lake Tecocomulco (73), silicic volcanic rocks exposed within the catchment of ancient Lake Gale could have contributed the detrital tridymite and cogenetic material to the Murray formation. Fine-grained sediments are most readily formed by downstream fining in alluvial settings, and evidence for this is preserved in the Gale crater moat (74). The even and fine lamination observed in the Murray formation at Marias Pass is inconsistent with direct fallout of ash or equivocally even though a water column (1). For the lower Murray formation at Pahrump Hills, these regular laminae were interpreted to result from the settling of fines derived from deltaic deltas, likely as plumes (1). Therefore, we suggest that the tridymite-bearing material was derived by erosion and transport from a silicic source area in a manner similar to Lake Tecocomulco. Unlike the Lake Tecocomulco analog, which has units of interstratified silicic volcanic ash (73), there are no known silicic volcanic rocks interstratified with Gale sedimentary rocks, so we appeal to crater rim and central peak regions as sources of tridymite-bearing material that may predate the Gale crater impact.

Recent studies have suggested that the Gale crater rim/wall may host igneous lithologies more evolved than other known Martian igneous rocks, ranging up to ~67 wt. % SiO₂ (75). The Lake Gale basin would have captured sediments from these terrains. Mineralogical observations across Mars made by orbital remote-sensing have also been interpreted as evidence for magma evolution to compositions more silicic than basaltic (76–78). The microclast in the ureilite meteorite EET 87720, which has a Buckskin-like mineralogy and composition, is also consistent with an evolved magma on a parent body that is possibly Mars (78).

The mixed-cation salts, minor oxides, and any precipitated silica in Buckskin amorphous material can be interpreted as cements precipitated during deposition and/or from later infiltrations by aqueous solutions having variable chemistries, temperatures, and acidities. The crystalline cation-deficient magmatic could also be present as a primary precipitate and cement, but there are insufficient constraints available to exclude igneous detritus or diagenesis of Fe-bearing materials. Anhydrite is interpreted as late fracture and vein fill as reported for other drill samples (8), implying its precipitation postdates lithification of the tridymite-bearing sedimentary rock.

The origin of the opal-A is not constrained. It could have formed as an alteration product of high-SiO₂ volcanic glass, as a residue from acid sulfate leaching of silicates in the sediment source region, or as similar residue from leaching in the sediment itself. Another alternative is primary precipitation of silica gel in the Gale lake environment followed by diagenesis to opal-A and opal-CT after burial. CheMin would not be able to distinguish between silica gel and opal-A, however (SI Appendix, Fig. S6). At present, there are insufficient constraints to partition the high-SiO₂ amorphous material among the aforementioned possible formation pathways, although silicic volcanism and diagenesis can account for all opal-A and opal-CT.

Implications for Martian Petrogenesis

The Buckskin tridymitic mudstone sample contains abundant SiO₂ phases (~55 wt. % of bulk sample) consisting of 14 wt. % tridymite, 2 wt. % cristobalite, 6 wt. % opal-CT, 33 wt. % opal-A and/or high-SiO₂ glass, and no quartz. The monocrystalline tridymite is well crystallized and not a mineraloid, such as opal with partial tridymite stacking, which might be attributed to a low-temperature origin. Because the Martian crust is largely basaltic, we explored other options for the origin of Buckskin tridymite. Of all the options, derivation from silicic volcanic rocks is the most parsimonious within available constraints, the most important being its high formation temperature (~870 °C to ~1,470 °C).

Although the general view of Mars is that of a basaltic planet, tridymite at Buckskin adds support to previous studies that describe regions of Mars where occurrences of high-SiO₂ igneous rocks have been inferred (76–78). Furthermore, the Buckskin tridymitic mudstone is yet another indication of evolved volcanic compositions in sedimentary source regions of Gale crater (75). The unexpected discovery of tridymite at Gale crater is further evidence of the complexity of igneous petrogenesis on Mars, with igneous evolution to high-silica compositions.

ACKNOWLEDGMENTS

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Supporting Information Appendix

1. **Supporting Text.** Silica-rich terrestrial deposits without tridymite.

2. **Table S1.** Chemical compositions from Rietveld analysis and chemical composition of minerals used for calculation of summed chemical composition of crystalline material.

3. **Fig. S1.** (a) Elevation map of Gale crater showing location of geologic map (white box). (b) Geologic map with principal stratigraphic units.

4. **Fig. S2.** Generalized stratigraphy of bedrock exposed across Aeolis Palus (Bradbury group) and the lower part of Mt. Sharp (Murray formation).

5. **Fig. S3.** Comparison of Buckskin patterns from the summation of diffraction images 1-4 and 16-45.

6. **Fig. S4.** Individual diffraction patterns for each Buckskin crystalline mineral and fit (sum of individual mineral patterns).

7. **Fig. S5.** Diffraction patterns for the sum of amorphous and instrumental components, their individual patterns, and the Buckskin diffraction pattern.

8. **Fig. S6.** Transmission XRD patterns for high-silica amorphous materials.
Silica-rich terrestrial deposits without tridymite.

High-SiO₂ terrestrial environments where tridymite does not occur because sufficiently high temperatures are not present include hydrothermal and cryogenic silica sinter deposits (61-70). After initial deposition as colloidal opal-A, sinters undergo incremental and progressive mineralogical transformation in the sequence opal-A → opal-CT → opal-C → quartz with aging. Similarly, tridymite formation has not been reported in low temperature acid sulfate environments. Leaching of surface and near surface silicate country rock (New Zealand geothermal fields) by acid-sulfate steam produces high-SiO₂ residues, with the first-formed phase described as “disordered opal-A” (63, 69). The mineralogical aging sequence for the silica residues is described as opal-A → opal-CT → chalcedonic quartz. The maturation process was investigated experimentally at higher temperatures and pressures (430 °C and 31 MPa and circum-neutral pH) with silica polymorphs forming in the sequence amorphous-SiO₂ → cristobalite → quartz (70). In a field experiment, (65) reported that maturation of opal-A to quartz can be accelerated by acidic-steam condensate (pH = 3.5 – 5.5 and T = 74 – 94 °C).

Another type of high-SiO₂ deposit without reported tridymite is the hydrocarbon-bearing Athel Silicilyte (South Oman Salt Basin, Sultanate of Oman). This finely laminated sedimentary rock (mudstone) with up to 95 wt.% SiO₂ is interpreted (71, 72) as primary chemical precipitates of silica dissolved in evaporating seawater brines at temperatures too low (below 45 °C) for tridymite formation. Although the initial SiO₂ precipitate was likely colloidal or opaline silica, the Oman silicilyte is now chert (microcrystalline quartz) (72).
Table S1. Mineral compositions from Rietveld analysis and literature sources used for calculation of the summed chemical composition of Buckskin crystalline material.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tridymite</th>
<th>Cristobalite</th>
<th>Plagioclase</th>
<th>Sanidine</th>
<th>Magnetite</th>
<th>Anhydrite</th>
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<tr>
<td>SiO₂ (wt.%)</td>
<td>96.5±3.7</td>
<td>100.0</td>
<td>55.7±0.9</td>
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<td>TiO₂</td>
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<tr>
<td>Al₂O₃</td>
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<td>27.7±0.6</td>
<td>18.6</td>
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<tr>
<td>Cr₂O₃</td>
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<tr>
<td>FeO</td>
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<td>Fe₂O₃</td>
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<td>0.6±0.4</td>
<td>---</td>
<td>88.6</td>
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<td>MnO</td>
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<tr>
<td>MgO</td>
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<td>CaO</td>
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<td>Na₂O</td>
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<td>5.5±0.4</td>
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<tr>
<td>K₂O</td>
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<td>P₂O₅</td>
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<td>SO₃</td>
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<tr>
<td>Cl</td>
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</tr>
<tr>
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<td>100.0</td>
<td>100.3</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
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</tbody>
</table>

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*Uncertainties are 2σ.
†Tridymite from average of (13, 14); plagioclase from average high SiO₂ martian meteorites (15); sanidine from Webmineral (http://www.webmineral.com/); magnetite from refined unit cell parameters assuming only Fe²⁺ and Fe³⁺ are present (cation-deficient magnetite); cristobalite and anhydrite from stoichiometric compositions; no detected crystalline mineral has Cr₂O₃, MnO, P₂O₅, and Cl so that their concentrations in bulk sample are assigned to the Buckskin amorphous material; weight percentages of minerals in crystalline material are from Table 2.
Fig. S1. (A) Elevation map of Gale crater showing location of Geologic map (white box). (B) Geologic map with principal stratigraphic units of Aeolis Palus (Bradbury group) and foothills of Mt. Sharp (Murray formation), major study locations (Rocknest, Yellowknife Bay, Kimberley, Pahrump Hills, and Marias Pass), rover traverse, and landing ellipse. The Buckskin drill hole is located in the Marias Pass area (white box).
**Fig. S2.** Generalized stratigraphy of bedrock exposed across Aeolis Palus (Bradbury group) and the lower part of Mt. Sharp (Murray formation). See (1) for more detailed breakdown of depositional facies, and their interpretation as fluvial and lacustrine deposits. Drill holes are indicated by JK (John Klein) and CB (Cumberland) at Yellowknife Bay, WJ (Windjana) at Kimberley, CH (Confidence Hills), MJ (Mojave) and TP (Telegraph Peak) at Pahrump Hills, and BK (Buckskin) at Marias Pass. See Fig. S1 for geologic map.
**Fig. S3.** Comparison of Buckskin patterns from the sum of diffraction images 1-4 and 16-45. Both patterns are normalized to 45 total images (i.e., the same integration time). The diffraction peaks for tridymite and anhydrite decrease and increase in intensity, respectively, in pattern 16-45 versus 1-4. Diffraction patterns for individual crystalline minerals are shown at the bottom of the figure (offset and the most intense peak of each pattern normalized to the same value).
Fig. S4. Individual diffraction patterns for each Buckskin crystalline mineral and fit (sum of individual mineral patterns). The unit cell parameters of tridymite, plagioclase, sanidine, and magnetite were refined during the fitting procedure. Weight percentage of each mineral relative to crystalline material is given in parenthesis. Y-axis corresponds to the Fit pattern; other patterns are offset for clarity.
Fig. S5. Diffraction patterns for the sum of amorphous and instrumental components, their individual patterns, and the Buckskin diffraction pattern (sum of diffraction images 1-4). The pattern for opal-A + obsidian was used for purposes of modeling the high-SiO₂ amorphous material, but different combinations of other amorphous high-SiO₂ materials could have been used (e.g., silica glass and rhyolitic glass (Fig. S6)). The peak near 6.5° 2θ is from the Kapton cell window.
Fig. S6. Transmission XRD patterns for high-silica amorphous materials. Diffraction patterns were obtained on a CheMin-4 instrument that is the laboratory equivalent of the MSL CheMin instrument. Silica gel and silica glass (both synthetic) are nominally 100 wt.% SiO$_2$ on a water-free basis. Libyan desert glass and Wabar impact glass (Saudi Arabia) are high-SiO$_2$ glasses formed by meteoritic impact into desert sands. Silica sinter (New Zealand), gem opal (Australia), and the residue of acid-sulfate leaching (Hawaii) all have diffuse diffraction peaks centered near 26° 2θ equivalent to opal-A or synthetic SiO$_2$ glass. The position of the diffraction peak maximum increases with decreasing SiO$_2$ concentration from rhyolitic (New Mexico) to ~31° 2θ for Gusev basaltic glass (synthetic). The acid-sulfate residue and the rhyolite patterns have minor diffraction peaks from anatase and quartz, respectively. Gusev glass was used as the model for the amorphous material for Rocknest soil and the John Klein, Cumberland, and Windjana drill samples (7-9). Peaks denoted by arrows are instrumental artifacts.