MARTIAN GEOLOGY

Brine-driven destruction of clay minerals in Gale crater, Mars


Mars’ sedimentary rock record preserves information on geological (and potential astrobiological) processes that occurred on the planet billions of years ago. The Curiosity rover is exploring the lower reaches of Mount Sharp, in Gale crater on Mars. A traverse from Vera Rubin ridge to Glen Torridon has allowed Curiosity to examine a lateral transect of rock strata laid down in a martian lake ~3.5 billion years ago. We report spatial differences in the mineralogy of time-equivalent sedimentary rocks <400 meters apart. These differences indicate localized infiltration of silica-poor brines, generated during deposition of overlying magnesium sulfate-bearing strata. We propose that destabilization of silicate minerals driven by silica-poor brines (rarely observed on Earth) was widespread on ancient Mars, because sulfate deposits are globally distributed.

Brucite and smectites are a group of clay minerals characterized by high surface areas and negative electrostatic charge (1). These properties promote intimate associations with organic material during sedimentation, enhancing organic preservation in Earth’s geological record (2). The increased temperature and pressure experienced by sediments during burial cause physical, chemical, and mineralogical changes—collectively termed burial diagenesis—that break down mineral–organic associations. A common burial diagenetic change observed on Earth involves the transformation of smectite into other minerals (typically illite and chlorite), a process that coincides with molecular reconfiguration and degradation of associated organic matter (1). On Mars, Noachian- to Hesperian-age (~4.1 to 3.2 billion years ago) sedimentary rocks that contain smectites but lack evidence for these transformations could therefore preserve information on geological or astrobiological processes (2, 3).

Since landing in Gale crater in 2012, the Curiosity rover has traversed ~25 km across the crater floor and the base of Aeolis Mons (informally called Mount Sharp), a 5.5-km-high mountain in the center of Gale. Rover measurements have revealed smectite-bearing ~3.5-Ga sedimentary rocks with vertical thicknesses of several hundred meters (Fig. 1). The smectites in these rocks are largely unaffected by burial diagenetic transformations observed in sedimentary basins on Earth and preserve organic compounds (4–6). Bulk geochemical indices and mineralogical trends in these rocks predominantly reflect depositional processes and conditions, as they coincide with sedimentary indicators of changing environments within the lake system that once occupied the crater floor ~3.5 Ga (5, 7–9).

Despite the limited evidence for burial diagenesis of clay minerals, outcrops surveyed by Curiosity display the influence of reactions involving liquid water (aqueous alteration) that postdate sediment deposition (and are therefore referred to as diagenetic reactions). Networks of millimeter- to centimeter-scale, calcium sulfate–filled fractures and veins are frequently found penetrating host rock (4, 10). In some cases, the passage of fluids has altered the mineralogy and geochemistry of host sediments, producing decimeter-scale “alteration halos” adjacent to fractures (11). Some rocks along Curiosity’s traverse experienced enhanced mobilization of trace elements and mineralogical reactions that influence the physical and spectral properties of rocks (12–16). X-ray amorphous materials have been detected in all samples analyzed with the rover’s CheMin x-ray diffraction (XRD) instrument, with abundances of ~15 to 70 wt %. This material could be the product of multiple episodes of aqueous interaction with sediment (11, 13, 17). Radiometric dating of jarosite—a potassium-bearing, iron-sulfate mineral—provides evidence for intermittent aqueous alteration extending over a period of at least half a billion years following deposition (18).

The protracted history of diagenetic reactions in Gale crater has made it challenging to identify the sources and drivers of the post-depositional passage of fluids (13–15). Natural variations in the depositional mineralogy of sediments, a function of changing sediment sources, depositional setting, and lake conditions (9), make the task more difficult. We attempt to eliminate this extra complexity by examining the influence of diagenetic reactions on the mineralogy of a lateral transect of ancient lake mudstones, deposited in similar environments at the same time.

Study area

Glen Torridon (GT) is a shallow west-to-east elongated trough ~0.3 to 1 km wide, lying between the slopes of Aeolis Mons to the south and the more resistant rocks of Vera Rubin ridge (VRR) to the north (Fig. 2). Rocks exposed within GT exhibit deep near-infrared absorption features in orbital reflectance spectra, which are attributed to smectites (9, 20). The clay minerals in GT are part of a sequence of remotely detected hydrous and hydroxylated minerals exposed on Aeolis Mons. These clays are overlain by rocks enriched in sulfates and iron oxides (19, 20), a sequence that is widely observed on Mars and is thought to have formed during exhaustion of the planet’s near-surface liquid water (3, 21).

Two main geomorphological subunits in GT were identified from orbital imagery before Curiosity reached GT in January 2019: a smooth-ridged unit to the north, skirting VRR, and a fractured unit to the south (Fig. 2). During Curiosity’s traverse, rover imagery showed that the smooth-ridged unit is covered by a mixture of pebbles and sand. Occasional outcrops expose thinly to thickly laminated mudstones, which are sometimes fractured and rubby (the likely source of the pebbles) and sometimes exhibit alternating recessive and resistant laminations. The overlying fractured unit primarily consists of sandstones. The rock compositions and their physical features (which, when grouped together, define a distinguishable rock unit or facies) resemble underlying and laterally equivalent deposits (8, 22, 23), indicating the continued presence of a lake with intermittent episodes of deposition by rivers and of wind-blown sediment. Our analysis of rover imagery shows no evidence of faulting or a depositional break marking the boundary between VRR and GT.
The flat-lying bedding of the rocks, and the geomorphology of the GT topographic trough, mean that strata exposed in GT are lateral equivalents of the Jura member exposed on the north face of VRR (Fig. 2) (24). This is confirmed by our identification of distinctive rocks of the “Fodgarry facies” that can be traced from GT to VRR (Fig. 2). Therefore, GT mudstones correspond to the Jura member of the Murray formation, and overlying sandstones make up the Knockfarril Hill member (Figs. 1 and 2).

*Curiosity* drilled a pair of rock samples, informally called Aberlady (AL) and Kilmarie (KM), from laminated mudstones of the Jura member of the Murray formation exposed in GT. A second pair of drilled samples from GT [Glen Etive (GE) and Glen Etive 2 (GE2)] were collected from the Knockfarril Hill member (Fig. 1 and 2). We analyzed the GT samples (25) and their VRR counterparts from the Jura member [Rock Hall and Highfield (14, 15)] to compare the mineral and geochemical properties of sedimentary rocks that share the same depositional history.

X-ray diffraction and evolved gas analysis

Mineralogical analyses of GT samples, using the CheMin instrument (25), show that they contain many of the phases identified in other Murray formation sediments (Table 1 and Fig. 2) (5, 12–14). GT samples contain clay minerals, plagioclase feldspar, calcium sulfate minerals (bassanite and anhydrite), and an X-ray amorphous component in abundances >5 wt %.

Minor constituents (<5 wt %) include hematite, pyroxene, and in KM and GE2, siderite (iron carbonate) (Table 1 and Fig. 2). The presence of carbonate minerals has been inferred from CO2 released by rock samples in evolved gas analysis (EGA) experiments performed by the Sample Analysis at Mars (SAM) instrument on *Curiosity*, before the rover’s arrival at GT (26). However, carbonates have not previously been definitively observed in CheMin data, indicating abundances below the instruments’ detection limit of ~1 wt %.

In KM, we detect multiple diffraction peaks from below the detection limit of ~1 wt %.

We characterize clay minerals in rocks from GT using the position and breadth of XRD peaks, coupled with H2O-release temperatures of structurally bound hydroxyl groups (the process of dehydroxylation) derived from SAM EGA experiments (25). As much of the Murray formation, low bulk potassium content (table S1) and a broad XRD peak at low angles (the 001 peak in Fig. 3), corresponding to the ~10-Å spacing of clay mineral layers (known as the basal reflection), indicate the presence of smectite with collapsed interlayers, expected under the low-humidity conditions inside CheMin (4, 5, 27). SAM EGA experiments on KM and GE2 reveal H2O-evolution temper-atures of ~400° to 600°C (Fig. 4), consistent with dehydroxylation of a Fe3+-rich dioctahedral smectite (28). However, H2O lost in this temperature range could also arise from x-ray amorphous materials (28). The position of an XRD peak related to the size of smectite crystals along the b axis (the 02l peak) is sensitive to the occupancy and types of cations within smectite octahedral sheets (4, 5, 27). 02l peak positions from GT samples (Fig. 3) are consistent with a Fe3+-rich dioctahedral smectite. The unit cell lengths of GT smectite crystals along the b axis were calculated from XRD data (25) and range from 9.081 to 9.112 Å (table S2). We estimate an iron content of ~0.9 to 1.2 atoms per formula unit (table S2), using previously published empirical relationships (29), which is approximately half of the dioctahedral cation sites.

The XRD data for KM contain another low-angle peak, corresponding to an interplanar spacing of ~9.22 Å (Fig. 3), not previously observed in *Curiosity* drilled or scooped samples. This peak is in a region typically occupied by basal reflections of clay minerals (7). However, the width of the peak is equivalent to the angular resolution of the CheMin instrument (fig. S2) and is considerably sharper than the smectite basal reflection in the same sample (Fig. 3), as well as other smectite-bearing samples from Gale (4, 5).

After eliminating other candidate phases, including hydrated iron sulfates, phosphates, and zeolites (25), we interpret this peak as arising from a mixed-layer serpentine-talc (S-T). S-T is a clay mineral in which layers of talc and serpentine are interstratified with each other. We fitted the peak positions and relative intensities in the KM data with a one-dimensional XRD model of S-T, finding a best-fitting composition of mixed-layer Fe3+-bearing talc containing ~6% serpentine (25). An EGA H2O release at ~715°C—lower than observed in talc lacking Fe3+ substitution—supports this interpretation (Fig. 4). S-T constitutes ~10% of the total clay mineral component in KM (25). Mutated peaks at 9.22 Å in the XRD data of other GT samples indicate that they contain S-T in smaller amounts (Fig. 3).

Origin of mixed-layer serpentine-talc

On Earth, talc forms in a variety of geological settings, as an aqueous alteration product of the presence of smectite with collapsed interlayers, expected under the low-humidity conditions inside CheMin (4, 5, 27). SAM EGA experiments on KM and GE2 reveal H2O-evolution temper-
magnesium-rich, silica-poor mafic and ultramafic volcanic rocks, as well as magnesium-rich sedimentary precursors (typically carbonates). Fe²⁺ substitution in talc (as inferred for KM) is usually characteristic of volcanic precursors (30). Talc can form directly from olivine and pyroxene in mafic and ultramafic volcanic rocks subjected to subsurface hydrothermal alteration, and in surficial weathering environments (31, 32). From the chemical composition, mineralogy, and the degree to which sedimentary textures are preserved in GT, we infer that in situ S-T production within GT rocks is unlikely (see supplementary text). Instead, we suggest that S-T (a minor phase in GT rocks) was transported into Gale crater as sedimentary detritus, derived from erosion of older bedrock. As discussed below, our proposed origin of S-T is unlike that of smectites found in the same samples and in rocks from older stratigraphic levels, which likely formed close to the time of deposition of sedimentary strata (4, 5, 27).

Although we cannot exclude inputs of hydrothermal talc derived from basaltic rocks in Gale’s catchment, any such sources would also have contributed chloritized aluminum-bearing phyllosilicates, zeolites, and amphiboles to GT rocks (27, 31)—minerals that have not been identified in Curiosity data. Although mixed-layer S-T is rarely reported on Earth, it occurs as a retrograde product of metamorphosed ultramafic rocks (33) and forms during synthesis of serpentine minerals under experimental hydrothermal conditions (34). These results lead us to hypothesize that inputs of S-T to GT sediments were derived from ultramafic

Fig. 2. Mineralogical, geochemical, stratigraphic, and geomorphologic overview of the areas of VRR and GT explored by Curiosity. (A) Mosaic of orbital images (in visible wavelengths) of VRR and GT (40) showing the rover path (white line), entering from the top left of the image, and progressing to GE in the southeast (SE). Drill locations along the path are indicated with white numbered circles. The numbers correspond to bar charts showing the abundances of clay minerals as well as iron oxide, oxyhydroxide, and sulfate minerals derived from CheMin data. ChemCam measurements of rock lithium abundances, a proxy for clay mineral content (40), are shown as small colored circles (see color bar). The straight yellow line shows the position of the cross section in (B). Dashed yellow lines trace the boundaries between stratigraphic units. (B) Stratigraphic cross section showing the surficial expression of Murray formation members (colored bands) and the approximate orthogonal projection of the drill sample locations marked as circles. The vertical exaggeration is 2.1. mbr, member.
lithologies in Gale’s catchment transported to the crater floor by rivers.

Talc- and serpentine-bearing ultramafic rocks are products of serpentinization reactions, which generate free \( \text{H}_2 \) and methane (both greenhouse gases on Mars) and sequester inorganic carbon as carbonate minerals (35). The production rate of \( \text{H}_2 \) and hydrocarbons varies considerably, depending on mineral-reaction pathways (36). Local physicochemical conditions affect the potential astrobiological relevance of these environments (37). We can neither identify nor examine the source of S-T in Gale’s catchment, so it cannot assess its habitability. Nevertheless, our results indicate that serpentinization of ultramafic rocks took place in the vicinity of Gale prior to deposition of GT sediments at \( \sim 3.5 \) Ga.

**Origin of smectite**

The rover data on the composition, structural state, and abundance of clay minerals confirm orbital data that indicated Fe\(^{3+}\)-rich smectite is present along and adjacent to the rover traverse path through GT (19). The orbital detections were based on absorption features in reflectance spectra, including one arising from Fe\(^{3+}\)-OH vibrational modes centered at \( \sim 2.28 \) to \( 2.29 \) \( \mu \text{m} \) (19). The \( \sim 2.28-\mu \text{m} \) feature also exhibits a weak absorption at \( \sim 2.2 \mu \text{m} \), which was assigned to Al-OH vibrations (19). The latter feature was originally interpreted as either (i) the presence of a second phase, such as montmorillonite or poorly crystalline kaolinite, or (ii) the presence of Al\(^{3+}\) in octahedral sites of a ferri smectite. The second interpretation is consistent with the \( b \) axis crystal cell dimensions of smectite that we derived from the XRD data.

Orbital spectral absorptions attributed to clay minerals were weaker and less spatially coherent in Murray formation strata traversed by Curiosity prior to arrival at GT (5). Nevertheless, previous samples analyzed by ChemCam commonly contained smectite, with abundances of up to 28 wt % (5, 12–14). Earlier in the mission, smectite was also found in the older Sheepbed mudstone of the Yellowknife Bay formation (4, 27) (Fig. 1). The chemistry of smectite in Gale crater is variable: magnesium-rich trioctahedral varieties are found in the Karasburg member of the Murray formation rocks (Fig. 1), but smectites become increasingly rich in dioctahedral cations (Al\(^{3+}\) and Fe\(^{3+}\)) at higher stratigraphic levels, approaching VRR (5, 13, 14). Dioctahedral smectite is thought to be a product of oxidative chemical weathering in sediment source areas, during transport, or on the lake floor (5, 7). This hypothesis is supported by reductions in the mafic mineral content of dioctahedral smectite-bearing sediments compared to underlying rock strata, sedimentological evidence of episodic lake desiccation, and bulk chemical signatures of weathering-related element mobilization (5, 7).

The bulk mineralogy, geochemistry, and depositional environment of GT rocks are similar to those of the underlying members of the Murray formation, and therefore we propose a similar origin for the Fe\(^{3+}\)-rich smectite in GT. Variations in the iron, aluminum, and magnesium content of smectites are commonly observed in Earth lake systems—a consequence of variable lithologies and extent of weathering of catchment rocks, as well as processes that may modify the chemistry of clay minerals once they are deposited in the lake (38, 39). The detection of S-T indicates that one possible cause for the higher abundance of iron in GT smectite compared with other parts of the Murray formation is a change in sediment provenance, with increasing smectite contributions from well-drained mafic or ultramafic rocks. An alternative is that clay minerals in GT sediments were not subject to processes capable of enriching smectite in magnesium and aluminum at the expense of iron, as documented in other parts of the Murray formation (5, 13). The absence of trioctahedral smectites, and the lack of sedimentological evidence of desiccation seen in stratigraphically lower parts of the Murray formation, both support the latter hypothesis.

**Diagenetic drivers**

Textural, mineralogic, and geochemical observations from Curiosity have shown that VRR experienced enhanced alteration and cementation, making these rocks harder than other Murray formation exposures (14, 15). Heterogeneities in the color (red, purple, gray) and spectral properties of VRR rocks are observed cross-cutting the primary bedding and are attributed to enhanced crystallization of hematite (15). Centimeter-scale iron-poor halos surround iron oxide–rich, dark-toned diagenetic features and crystal pseudomorphs resembling gypsum (15, 16). Overall, the bulk chemistry of VRR is like that of the rest of the Murray formation, but diagenetic features and geochemical variability observed across the ridge indicate that elements, including iron, were locally remobilized (15, 16, 40). Several models have been proposed to explain the enhanced alteration of VRR (15). Most argue that VRR rocks were preferentially infiltrated by late diagenetic fluids, with flow focused along the contact between the Murray formation and a younger rock unit called the Stimson formation (Fig. 1).

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**Fig. 3.** XRD data from GT drill samples AL, KM, GE, and GE2. The peaks of clay minerals and other major mineral components are labeled and marked by dashed vertical lines. An, anhydrite; B, bassanite; P, plagioclase feldspar; S, siderite. KM data show a peak at \( \sim 11.1 \) \(^{\circ}\) (\( \sim 9.22 \) \( \AA \)), which we interpret as a mixed-layer serpentine-talc (25). Data have been arbitrarily shifted vertically for display. XRD data were collected by using Co K\(_\alpha\) radiation (25).
Hypothesized fluid sources include (i) heated water migrating from the deeper parts of the crater or (ii) gravity-driven regional subsurface hydraulic systems with flow from Mars’ southern highlands to the northern lowlands (14, 15).

The types of minerals and their abundances in GT and VRR rocks sampled from the same stratigraphic interval provide evidence that the escarpment between GT and VRR marks a diagenetic front (14, 15). GT drilled samples have clay mineral contents of 26 to 34 wt % (Table 1), compared to 5 to 13 wt % in VRR (14) (Fig. 2). Iron oxide and oxyhydroxide abundances show an opposite trend, with levels of 9 to 16 wt % in VRR samples (14) compared to ≤2 wt % in GT (Table 1 and Fig. 2). Unlike VRR samples, akaganeite, jarosite, or opaline silica were not detected in GT samples (14). Abundances of lithium, measured by the ChemCam instrument using laser-induced breakdown spectroscopy (25), provide a proxy for clay mineral content of rocks (40). Thousands of ChemCam data points collected across VRR and GT confirm that the drilled samples are representative of the differing clay mineral content of GT and VRR rocks (Fig. 2). These chemical and mineralogic differences cannot be explained by depositional processes, such as hydrodynamic sorting or variations in sedimentary sources, because of the stratigraphic equivalence of the units in immediately adjacent areas (Fig. 2).

Comparisons of GT and VRR mineralogy provide additional constraints on the diagenetic history of VRR. Our analysis and interpretation of GT clay minerals show that Fe²⁺-rich smectites and Fe³⁺-bearing S-T, originally deposited in lake sediments, were converted to iron oxides, oxyhydroxides, and opaline silica in VRR. A partially analogous reaction pathway is commonly observed in Earth weathering environments, where rainwater infiltrates soils, preferentially leaching silicon from smectite, forming iron oxides and aluminum-rich materials, such as allophane or kaolin group clay minerals (32). However, the lack of vertical elemental and mineralogical gradients shows that VRR has not experienced top-down weathering (15). Destruction of smectite during burial and diagenesis is rarely observed in Earth sedimentary basins, because of the strong influence of silica activity on the thermodynamic stability (fig. S3). Siliceous materials filling sedimentary basins typically keep fluids enriched in silica, which may lead to the precipitation of additional clay minerals as cements during burial and lithification of porous sedimentary rocks (1). The subsurface sources of late diagenetic fluids proposed to account for alteration at VRR (14, 15) would also likely be high in silica through buffering with basalts and basaltic detritus (41) and thus cannot account for the destabilization of smectites. Another mechanism and source of fluids is required.

**Brine-driven diagenesis**

We propose that the conversion of Fe³⁺-smectites and Fe²⁺-substituted S-T into iron oxides and oxyhydroxides in VRR involved density-driven circulation of oxidizing, silica-poor brines (fig. S3) originating from the overlying sulfate-bearing unit (SBU) previously identified in orbital observations. The mode of deposition of the SBU cannot be determined from orbital data, and Curiosity is in the early stages of investigating the SBU. However, as indicated by the lateral extent of SBU exposures around Mount Sharp and the correspondence of orbital mineral variation to bedding, the SBU (or parts of it) could be a continuation of the lacustrine conditions within Gale, albeit with a shift in climatic and/or local hydrological conditions that led to the deposition of magnesium sulfate minerals (19, 20).

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**Table 1. Mineralogical composition (wt %), with 1–σ errors, of drill samples from GT (Fig. 2).** AL and KM are part of the Jura member. GE and GE2 come from the Knockfarill Hill member (Fig. 1). The detection limit for crystalline materials is ~1 wt %.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Kilmarie</th>
<th>Glen Etive</th>
<th>Glen Etive 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andesine</td>
<td>7.8 ± 0.9</td>
<td>11.4 ± 0.8</td>
<td>23.5 ± 1.1</td>
</tr>
<tr>
<td>Hematite</td>
<td>0.9 ± 0.4</td>
<td>2.0 ± 0.7</td>
<td>1.5 ± 0.5</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Trace</td>
<td>Trace</td>
<td>–</td>
</tr>
<tr>
<td>Ca sulfate</td>
<td>9.4 ± 0.3</td>
<td>10.4 ± 0.4</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>Sanidine</td>
<td>Trace</td>
<td>1.4 ± 0.7</td>
<td>2.4 ± 0.6</td>
</tr>
<tr>
<td>Pyroxene</td>
<td>3.2 ± 1.1</td>
<td>1.6 ± 0.5</td>
<td>4.2 ± 1.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>Siderite</td>
<td>1.9 ± 0.2</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>Clay minerals</td>
<td>28 ± 5</td>
<td>34 ± 6</td>
<td>26 ± 5</td>
</tr>
<tr>
<td>Amorphous</td>
<td>48 ± 24</td>
<td>38 ± 19</td>
<td>37 ± 18</td>
</tr>
</tbody>
</table>
Orbital sulfate detections could also originate from sulfate-cemented clastic sedimentary rocks deposited in aqueous or eolian settings (19).

Irrespective of the mode of deposition, orbital observations of the ~400-m-thick SBU show that it is associated with spectral absorptions consistent with mono- and polyhydrated magnesium sulfates (19, 20). These magnesium sulfates are highly soluble, and their precipitation requires intense evaporative concentration and the formation of dense brines (42). Combined with orbital data indicating possible conformable relationships with underlying perennial lake sediments, the thickness and areal extent of the SBU imply that density-driven brine infiltration likely occurred prior to the lithification of the Murray formation. This process is observed on Earth (43, 44). For example, in the Tyrrell Basin of southeastern Australia, evaporative brines generated in salt lakes have infiltrated tens of meters into underlying freshwater lake sediments over the last ~30,000 years, in response to changing climate (44).

Sulfate-dominated brines that evolve in saline lake systems on Earth tend to maintain neutral to slightly acidic pH (45). This allows brines to become depleted in silica through precipitation of amorphous silica, clay minerals, and feldspars as brines are progressively concentrated (46, 47). In the Lake Lewis Basin, central Australia, a climate-induced change from hydrologically open conditions to a closed salt-lake system resulted in the infiltration of brines into older, clay-mineral-rich, perennial lacustrine sediments (46). Brines beneath the dry lake are depleted in silica (<10 parts per million), resulting in the destabilization of detrital aluminosilicate components of older perennial deposits, including feldspar and smectite, and transformation into substantial portions (up to ~30 w %) of x-ray amorphous aluminosilicate materials (46). Therefore, we propose that the most concentrated brines generated during the deposition of the SBU could have also been depleted in silica and capable of destabilizing smectites and S-T. Exposure to oxidized brines, descending from the near-surface, provided an additional driver promoting the alteration of Fe$^{3+}$-substituted S-T.

Brine-driven diagenesis is predicted to be heterogeneous (43, 46). On Earth, concentrated brines develop by progressive evaporation of fresher waters that migrate from marginal areas of sedimentary basins to the center. This process produces strong lateral gradients in aqueous geochemistry that follow chemical pathways governed by the initial water chemistry and precipitation of minerals during migration (45). Geochemical gradients may be preserved in the rock record as spatially distinct mineral facies (43). The position of mineral facies boundaries can vary stratigraphically, in response to the migration of the depocenter and changing hydrological conditions (49).

In Gale, the most concentrated brines would have been spatially restricted to topographic lows on the crater floor at any given time and migrated in response to variations in sediment supply and freshwater recharge. The interactions of brine with underlying perennial lacustrine sediments likely occurred before substantial burial, at temperatures of less than 50°C. Under these conditions, the nature and extent of mineralogical reactions would have been subject to kinetic controls and might not have reached equilibrium. For example, recrystallization of a secondary clay mineral after smectite dissolution may have been prevented by a combination of short residence of fluids and fast iron oxide and amorphous aluminosilicate precipitation. Reaction kinetics could have been governed by local variations in the geochemistry of interstitial fluids, as well as the composition and physical properties of sediments, such as permeability and surface area. Thus, the inherent heterogeneity of brine-driven diagenesis accounts for lateral differences in the conversion of clay minerals to iron oxide and oxhydroxide in GT and VRR. This heterogeneity could also explain the localized mobilization and recrystallization of iron observed on VRR, through complexation of iron with highly concentrated SO$_4^{2-}$ and possibly (based on the presence of the mineral akaganite) Fe$^{2+}$-rich brines (13, 14, 16).

**Other evidence for the influence of brines**

The influence of descending brines on other intervals of the Murray formation appears to be more pervasive than previously documented. Heterogeneous, low-temperature interactions of descending brines provide a plausible explanation for the co-occurrence of clay minerals to iron oxide and oxhydroxide in GT and VRR. This heterogeneity could also explain the localized mobilization and recrystallization of iron observed on VRR, through complexation of iron with highly concentrated SO$_4^{2-}$ and possibly (based on the presence of the mineral akaganite) Fe$^{2+}$-rich brines (13, 14, 16).

**Implications for the martian sedimentary record**

Tectonically driven subsidence and burial are the main drivers of diagenesis in sedimentary basins on Earth. Mars' sedimentary record has been preserved by the lack of tectonics, lower geothermal gradients, and timing of desiccation of the planet, which limited aqueous mineral reactions (3). The global, but temporally discrete, distribution of sulfate deposits on Mars is thought to record this desiccation process (27). Evidence for top-down diagenesis by infiltration of brines in Gale crater, combined with the global distribution of sulfates produced by Mars' shrinking hydrological budget, raise the possibility of more widespread alteration of older clay-mineral-bearing sediments through a mechanism that is rare on Earth. Brines can destabilize clay minerals and destroy intimate associations with organic molecules, potentially reducing the preservation capacity of the rock record. However, subsequent reabsorption on sulfates may be an efficient check on organic decay (50). Although brine-driven destruction of clay minerals complicates geological interpretation, water released during this process would have acted as a negative feedback, slowing the pace of planetary desiccation and potentially extending...
the period in which Mars had surface liquid water.

REFERENCES AND NOTES

25. Materials and methods are available as supplementary materials.

ACKNOWLEDGMENTS

We thank R. Kleeberg for help developing the CheMin instrument profile model for BGMN and A. Derkowski for informative discussion. J. C. Corona kindly provided XRD data from Fe talc, and P. De Decker shared knowledge of Australian lakes. We thank J. Bishop and two anonymous reviewers for helping improve the manuscript. We acknowledge the support of the Jet Propulsion Lab engineering and management teams and MSL science team members who participated in tactical and strategic operations, without whom the data presented here could not have been collected. Funding: Some of this research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (NASA), A.A.F., A.C.M., and C.M.F. acknowledge funding by the MSL Participating Scientist Program, NASA solicitation NNH15ZDA001N. J.F. acknowledges support from the Carlsberg Foundation. J.P.G. received additional funding from the Simmons Collaboration for the Origin of Life. Author contributions: T.F.B. wrote the manuscript, with corrections, discussions, and/or revised text from coauthors. J.C. led one-dimensional modeling of clay minerals, S.I.C. quantified the abundances of clay minerals and the x-ray amorphous phase from CheMin XRD data. G.W.D. led efforts to identify the 9:2:2-A phase from XRD data. C.M.F. led efforts to establish the relationships between rock strata exposed at VRR and GT, capturing them in Figs. 1 and 2. J.F. analyzed ChemCam Li data and helped produce Fig. 2. A.C.M. led the interpretation of SAM EGA data and helped produce Fig 4 and fig. 5A. A.S.Y. compiled the bulk geochemical data from the Alpha Particle X-ray Spectrometer shown in table S1 and used to generate fig. 5S. R.V.M. compiled the XRD data used to determine the angular resolution of the CheMin instrument (fig. S2). R.E.M. led comparisons of orbital and ground-based mineral data. C.N.A., T.F.B., D.W.M., S.M.M., E.B.R., M.T.T., V.T., and D.T.V. determined the abundances of crystalline phases in GT samples from XRD data. D.F.B., A.B.B., K.A.B., A.A.F., V.K.F., R.G., J.P.G., P.R.M., E.B.R., D.T.V., R.C.W., and A.R.V. designed the rover instruments and guided the mission. All authors performed operational roles in data collection. Competing interests: V.K.F. is also affiliated with the Department of Physics and Astronomy, Carleton College, Northfield, MN 55057, USA. Data and materials availability: All Curiosity data presented in this paper are archived in NASA’s Planetary Data System; the URLs and file identifications are listed in table S5. The software written by the authors of this paper and files needed to replicate the analyses are publicly available at Dryad (S1).

SUPPLEMENTARY MATERIALS

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