A Visit by Curiosity to Gale Crater’s Stratigraphic Record of Sulfate and Clay-mineral Deposition

D. Vaniman, MSL Landing Site Workshop, May 2011

Gamma-ray sulfur distribution at MSL field areas: It’s not just skin-deep.

*image adapted from McLennan et al., 2010, LPSC 41*
Curiosity’s Payload:
Ten instruments: All will provide information that pertains to mineralogy

**Imaging and Remote Analysis**
- **MARDI** – descent imaging/movie
- **Mastcam** – dual primary cameras; 440-1035 nm spectral range
- **ChemCam** – remote chemical analysis and spot imaging; 240-800 nm spectral range; ~50-225 µm laser spot size.

**Environmental Analysis**
- **REMS** – winds, temperatures, humidity
- **RAD** – radiation environment
- **DAN** – neutron detection of soil hydrogen

**Contact Analysis**
- **APXS** – alpha particle chemical analyzer
- **MAHLI** – ‘hand-lens’ detail imaging; primary LEDs at 380-680 nm spectral range, plus UV LEDs at 365 nm

**Internal Laboratory**
- **SAM** – spectrometry, chromatography, thermal analysis
- **CheMin** – mineralogy by X-ray diffraction and fluorescence
Five kilometers of strata are exposed in the Gale mound, but a key record is found in the lowest ~200 m.

Hydrous mineralogy of the lower mound includes smectite (nontronite) and Mg-sulfates (kieserite and polyhydrated).

Mineralogy and images from Milliken LSWG presentation, April 2010
The Promise of Gale (a working hypothesis)

• The sedimentary record of the lower mound captures a significant transition on Mars, from a relatively wet phyllosilicate-forming environment to a drier sulfate-forming environment.

• These sediments retain a decipherable record of that transition (i.e., they have not been modified to the extent that primary texture and mineralogy have been lost or completely overprinted).

• The deposits retain enough primary sedimentary or mineral-chemical information to identify what may have been a habitable environment.
Components of mineral evolution in the Gale Crater lower mound

• **Primary deposition**: to what extent were clay minerals and sulfates in aqueous communication? Could sedimentation have been so water-starved that some sulfates as well as phyllosilicates may be products of physical rather than chemical sedimentation?

• **Syndepositional to early post-depositional modification**: how much cementation or recrystallization?

• **Groundwater**: what was the paleohydrology of the deposits following initial formation – has the stratigraphy observed been entirely within the vadose zone since formation? Has perched or regional saturation altered the salt component and promoted salt-phyllosilicate reactions? What about subsurface ice?

• **Burial and exhumation**: did extensive burial of the lower mound sequence place these sediments in a $T^\circ\cdot P_{H2O}$ regime where dehydration and phase transformations would occur? Would retrograde products be expected on exhumation?

• **Weathering**: has long exposure to seasonal and obliquity cycles modified the sediments?
Mg-sulfate brine reactions with smectite: Cation exchange

- Palagonite, zeolites and smectites exchange their Ca for Mg in an Mg-sulfate brine; the result of this exchange is Ca-sulfate precipitation (either gypsum or bassanite) before Mg-sulfates precipitate. This process is most effective with smectites.
- If polyhydrated Mg-sulfates and/or kieserite at Gale formed from Mg-rich brines that interacted with smectite, gypsum or bassanite should be present.
- The amount of gypsum formed by cation exchange is variable but typically ~5% of the weight of nontronite. The XRD pattern below was collected by a lab instrument using Cu Kα radiation but is similar to what CheMin would observe.

![XRD pattern](image-url)
Brine reaction with smectite (Mg-sulfate brine/nontronite example): What to look for with MAHLI and with the ChemCam RMI
How about that kieserite?

• At low temperature, direct precipitation of kieserite may be possible, but only with an extremely evolved brine that leaves behind much more carbonate, Ca-sulfate, and chloride salts (R.J. Spencer, 2000). Not impossible at Gale, but not likely.
• The surest way to form kieserite is to expose a more hydrous Mg-sulfate to temperatures above ~50 °C.
• B.C. Hahn et al. (LPSC 42, 2011) estimate that with 5 km of sediment in Gale Crater the temperature at the bottom of the section would be ~75 °C.
• So . . . why isn’t it all kieserite?

*dunes*

erosional unconformity; lower unit mound is buried by upper mound-forming materials which will later erode away to make the mound we see today.

*Image from Edgett LSWG presentation, August 2010*
Playing field in the lower Gale mound for Mg-and Ca-sulfates: Whatever gets cooked will also cool off, with multiple retrograde reactions possible.

### Mg-sulfates

<table>
<thead>
<tr>
<th>Formula</th>
<th>Mineral name</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO₄ anhydrous</td>
<td>none (reagent)</td>
</tr>
<tr>
<td>MgSO₄·H₂O</td>
<td>kieserite</td>
</tr>
<tr>
<td>MgSO₄·H₂O type 2</td>
<td>none (reagent)</td>
</tr>
<tr>
<td>MgSO₄·2H₂O</td>
<td>sanderite</td>
</tr>
<tr>
<td>MgSO₄·2.4H₂O</td>
<td>none</td>
</tr>
<tr>
<td>MgSO₄·4H₂O</td>
<td>cranswickite</td>
</tr>
<tr>
<td>MgSO₄·4H₂O</td>
<td>starkeyite</td>
</tr>
<tr>
<td>MgSO₄·5H₂O</td>
<td>pentahydrite</td>
</tr>
<tr>
<td>MgSO₄·6H₂O</td>
<td>hexahydrate</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>epsomite</td>
</tr>
<tr>
<td>MgSO₄·11H₂O</td>
<td>meridianiite</td>
</tr>
<tr>
<td>MgSO₄·nH₂O</td>
<td>amorphous (n variable)</td>
</tr>
</tbody>
</table>

### Ca-sulfates

<table>
<thead>
<tr>
<th>Formula</th>
<th>Mineral name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO₄ anhydrous</td>
<td>anhydrite</td>
</tr>
<tr>
<td>CaSO₄·(&lt;0.8)H₂O</td>
<td>bassanite</td>
</tr>
<tr>
<td>CaSO₄·2H₂O</td>
<td>gypsum</td>
</tr>
</tbody>
</table>

**Diagram:**
- **Burial temperature of 348 K**
- **Approximate surface exposure conditions at present (TBD by REMS!)**

**Note:** The diagram shows a phase diagram for magnesium and calcium sulfates, indicating the stability fields and phase transitions under Martian conditions.
Detrital Mg-sulfates? How water-starved may the sulfate strata be?

- Polyhydrated sulfate strata of the lower and middle members have good expression of layering with marker beds that can be traced for several kilometers. These strata are probably a result of aqueous sedimentation and unlikely to be eolian.

- Aqueous transportation of detrital Mg-sulfate is very unlikely over short distances and probably impossible over kilometer distances (solubility of kieserite is 674 g/kg H₂O; contrast with gypsum at 2 g/kg H₂O).

- A possible “detrital” scenario would be to disperse eolian fine sand or silt laden with Mg-sulfates into a shallow lacustrine or playa system. (Detrital, but not for long!)

- In a wet system, we may not be able to determine ultimate sulfate origins.

“Sand makes me sad because it used to be big rocks . . . but not any more.”  

_Marge Simpson_
Did burial affect the clay minerals at Gale?

Marge might be sad about some of the clay minerals, too.

In the Delaware Basin, “It is not possible to characterize the original detrital components, especially the compositions of detrital clays, due to their alteration by later diagenetic processes.” (J.L. Krumhansl et al., 1990)

Diagenesis via Mg-rich brine transforms swelling clays (smectite) to forms with limited or no swelling capacity: e.g., mixed-layer chlorite/smectite, clinochlore, Mg-berthierine.

However, CRISM data reviewed by Milliken indicate that the major form of phyllosilicate at Gale is an Fe-rich swelling clay mineral, nontronite, and not a mixed-layer or chloritic form. Diagenesis is not indicated.

*Image from Milliken LSWG presentation, April 2011*
Recognition of primary vs. modified evaporite deposits

*after R.J. Spencer, 2000, RiMG 40 (Sulfate Minerals)*

• Primary or syndepositional textures and fabrics
  – Crystals rooted on substrate and growing upward
  – Detrital sediment covering crystal terminations, thick in low points and thin over high points
  – Accumulations of reworked detrital evaporite grains
  – Syndepositional dissolution-reprecipitation (e.g., late-stage cement; modified crystal terminations truncated and overlain by sediment)

• Alteration textures and fabrics
  – Evidence for disruption of sedimentary fabric
  – Polygonal or sutured mosaic textures
  – Vugs and veins with second-generation growth
  – Evidence of deformation (folding, flow-banding, pressure solution)

These features are mostly of mm to dm scale, readily examined by Mastcam, ChemCam RMI and LIBS, and MAHLI).
Post-exhumation history
Deliquescence/efflorescence with physical consequences

Mg- and Ca-sulfate efflorescence can produce crystallization pressures in the range of several tens of MPa.

Efflorescent sulfate salt crystallization in pores and fractures can disaggregate rock.

Recent work by Wilson and Bish has shown that in smectite-sulfate mineral mixtures, solid-state hydration produces cation exchange and sample expansion equal to or greater to that shown in slide 7 for nontronite in Mg-sulfate brine.

Solid-phase transitions such as this may account for localized slope degradation at Gale as observed by Dawn Sumner.

Image from S.A. Wilson and D.L. Bish, LPSC 2011 (RH cycling, 10% kieserite and 90% smectite)
Observations by Dawn Sumner

Is disruption localized on specific slopes a result of sulfate-phase efflorescence cycling?

Perhaps, but notably there is well-preserved layering in canyon walls that lacks visible evidence of salt disruption and may preserve pristine sedimentary strata ‘frozen in time.’

50m Scale Bar; 50m Contour Interval

*Image from Sumner LSWG presentation, April 2011*
Summary

- Gale Crater presents an opportunity to frame habitability in stratigraphic context. (Was there a habitable environment? If so, how persistent was it and how did it end?)

- If indeed benign smectite-forming environments present significant hope for finding organics, one of the challenges at Gale Crater will be to find the least compromised of smectite-rich strata. Strong indications for preservation of smectite at Gale argue that relatively uncompromised deposits occur. These are likely to be those deepest in the mound section, just beyond the landing ellipse.

- A significant goal at Gale Crater will be to identify pristinity of smectite strata as well as any brine reaction with or overprinting of smectite deposits. The mobile laboratory capabilities of Curiosity are up to this challenge.