
Introduction: Gale crater was selected as the landing site for the Mars Science Laboratory Curiosity rover because of orbital evidence for a variety of secondary minerals in the lower slopes of Aeolis Mons (aka Mount Sharp) that indicate changes in aqueous conditions over time [e.g., 1]. Distinct units demonstrate orbital spectral signatures of hematite, phyllosilicate (smectite), and sulfate minerals, which suggest that ancient aqueous environments in Gale crater varied in oxidation potential, pH, and water activity [e.g., 2, 3]. Vera Rubin ridge (VRR) is the first of these units identified from orbit to have been studied by Curiosity. Orbital near-infrared data from VRR show a strong band at 860 nm indicative of hematite [3,4]. Before Curiosity arrived at VRR, the hypotheses to explain the formation of hematite included (1) precipitation at a redox interface where aqueous Fe$^{2+}$ was oxidized to Fe$^{3+}$, and (2) acidic alteration of olivine in oxic fluids [3,4]. Studying the composition and sedimentology of the rocks on VRR allow us to test and refine these hypotheses and flesh out the depositional and diagenetic history of the ridge. Here, we focus on the mineralogical results of four rock powders drilled from and immediately below VRR as determined by CheMin.

CheMin Instrument and Sample Analyses at VRR: The CheMin instrument is an X-ray diffractometer and X-ray fluorescence spectrometer in transmission geometry with a Co X-ray source [5]. CheMin is located in the body of the rover and analyzes drilled rock powder or scooped loose sediment. Rietveld refinement of 1D diffraction patterns provides mineral abundances with a detection limit of ~1 wt.%.

CheMin analyzed four drilled rock samples during the VRR campaign: Duluth, from the Blunts Point member immediately below VRR, Stoen, from the Pettegrove Point member (the lowermost member of VRR), Highfield, from a gray portion of the Jura member (the uppermost member of VRR), and Rock Hall, from a red portion of the Jura member. All samples were drilled from laminated mudstone, interpreted as lacustrine deposits [6]. Each sample was analyzed by CheMin for a total of 22.5 hours. Most mineral abundances and unit-cell parameters of some abundant phases were derived from Rietveld refinements of 1D diffraction patterns using the MDI Jade software. Phyllosilicate and amorphous abundances were derived from FULLPAT analyses [e.g., 7]. Compositions of the X-ray amorphous components in each sample were estimated by subtracting the calculated composition of the crystalline component from CheMin from the Alpha Particle X-ray Spectrometer (APXS) compositions of the sample powders dumped from the drill stem [e.g., 8, 9].

Minerals and Amorphous Materials Identified by CheMin in VRR Samples: All four samples contain basaltic minerals (abundant plagioclase, minor pyroxene), hematite, Ca-sulfate minerals, phyllosilicates, and significant amounts of amorphous materials (~35-50 wt.% of each sample) (Fig. 1). There are important differences in hematite abundance and grain size, phyllosilicate abundance and structure, Ca-sulfate speciation, and the presence/absence of other secondary Fe(III) phases between the four samples. The secondary mineralogy of the four samples includes:

- **Duluth (below VRR, Blunts Point mbr).** Duluth contains minor amounts of hematite (~6 wt.% of the bulk) that display broad diffraction peaks, minor amounts of bassanite and anhydrite, ~15 wt.% phyllosilicate with a 10 Å basal spacing, and an amorphous component relatively enriched in FeO$_2$.

- **Stoen (lower VRR, Pettegrove Point mbr).** Stoen contains the most hematite in any sample drilled to date (~15 wt.%); minor amounts of jarosite, akaganeite, anhydrite, and gypsum; and ~10 wt.% phyllosilicate with a 9.6 Å basal spacing. The amorphous component is relatively high in MgO.

- **Highfield (upper VRR, gray Jura mbr).** Highfield contains abundant hematite (~9 wt.%), minor amounts of anhydrite and gypsum, trace amounts of bassanite, ~5 wt.% phyllosilicate with a 9.6 Å basal spacing, minor opal-CT, and an amorphous component relatively enriched in SiO$_2$.

- **Rock Hall (upper VRR, red Jura mbr).** Rock Hall contains minor amounts of hematite (~3 wt.%) and jarosite, but the most akaganeite drilled to date (~6 wt.%). Anhydrite is abundant and is the only Ca-sulfate mineral present. The sample contains ~13 wt.% phyllosilicate.
with a 9.6 Å basal spacing, and the amorphous component is relatively enriched in SO₄.

**Implications for the Aqueous History of VRR:**
The variety of secondary phases and differences in composition of the amorphous component among the four samples drilled on and immediately below VRR suggest a complex aqueous history. The abundance and grain size of hematite show significant variability on and below VRR. The breadth of hematite diffraction peaks in the Duluth pattern suggest a grain size of ~18 nm, based on Scherrer’s equation [10]. The concentration of FeO₃ in the amorphous component of Duluth also suggests the presence of nanophase Fe-oxides in that sample. The low angular resolution of CheMin does not allow us to constrain grain sizes >40 nm, but the indication of gray hematite in the Highfield sample from the Jura mbr suggests hematite grain sizes >3-5 μm in this sample [11,12]. Fe-rich hexagonal-shaped crystals in some Ca-sulfate veins in the Jura mbr are further evidence for coarse-grained hematite on VRR [13]. Coarse-grained hematite most commonly forms from fluids with elevated temperatures (~80-200 °C) [e.g., 12], although it can form under freezing conditions [14].

Phyllosilicate with a 9.6 Å basal spacing is consistent with (1) ferripyrophyllite, a member of the pyrophyllite-talc group, that commonly forms under slightly elevated temperatures (~55 °C) and saline conditions [e.g., 15], or (2) smectite altered by acidic fluids [16].

Akaganeite and jarosite identified in Stoer and Rock Hall suggest precipitation from acidic, saline fluids [17,18]. Abundant anhydrite and sulfate in the amorphous component of Rock Hall further indicate fluids with low water activity [e.g., 19].

Based on compositional and sedimentological data, we hypothesize that the sediments were deposited in a relatively oxic lacustrine environment, resulting in the alteration of mafic minerals and precipitation of nanophase Fe-oxides. Smectite may have formed in the lacustrine environment or during early diagenesis [e.g., 19,20,21]. After the rocks were lithified, we hypothesize multiple fluid episodes interacted with the rocks on VRR, causing the crystallization of hematite from nanophase precursors, altering smectite to form a 9.6 Å phyllosilicate, and precipitating akaganeite and jarosite. These fluids were locally acidic, saline, and/or warm and limited in their extent based on the sporadic detections of gray hematite, jarosite, and akaganeite. The unconformable contact with overlying sandstone of the Siccar Point group may have provided a conduit for multiple influxes of diageneric fluids.


Fig 1. Mineral and amorphous abundances derived from CheMin data for four samples drilled during VRR campaign, where DU = Duluth, ST = Stoer, HF = Highfield, and RH = Rock Hall. Samples are in stratigraphic order (i.e., Duluth is the lowest in the section).