MINERALOGICAL TRENDS OVER THE CLAY-SULFATE TRANSITION IN GALE CRATER FROM THE MARS SCIENCE LABORATORY CHEMIN INSTRUMENT.

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Introduction: The Mars Science Laboratory *Curiosity* rover landed in Gale crater in 2012 to explore a sedimentary sequence in lower Aeolis Mons (informally known as Mount Sharp) that shows changes in mineralogy from orbital visible/near-infrared reflectance spectroscopy [1]. Sedimentary layers with spectral signatures of hydrated Mg sulfate overly layers with signatures of Fe/Mg smectite, a mineralogical stratigraphy that is seen in other ancient sedimentary rocks across Mars [e.g., 2-4]. *Curiosity* recently completed its campaign in a valley with a strong orbital signature of smectite, named Glen Torridon. Mineralogical measurements by the CheMin X-ray diffractometer (XRD), complemented by evolved gas analyses by the Sample Analysis at Mars (SAM) instrument suite, allowed the identification of abundant Fe^{3+}-bearing dioctahedral smectite (i.e., nontronite) in Glen Torridon [5-6]. *Curiosity* left Glen Torridon in February 2021 and began traversing through a "clay-sulfate transition" zone on the way to the pediment and the sulfate unit [e.g., 7]. This clay-sulfate transition is defined in orbital reflectance spectroscopy as having a weak signature of hydrated Mg sulfate. *Curiosity* has drilled five outcrops over the traverse through the clay-sulfate transition and delivered the rock powders to CheMin for mineralogical analysis. Here, we report on the mineral assemblages of those five targets derived from CheMin XRD patterns and discuss mineralogical trends as the rover approaches the sulfate unit.

CheMin Analyses of Clay-Sulfate Transition Targets: The five rock powders analyzed by CheMin in the clay-sulfate transition, moving up section, include: Nontron (drilled at an elevation of -4073 m), Bardou (-4066 m), Pontours (-4041 m), Maria Gordon (-4015 m), and Zechstein (-3991 m). All were drilled within a portion of the Carolyn Shoemaker formation that has experienced such significant diagenetic alteration that sedimentary laminations have been obscured and overprinted. Diagenetic features along the transition include cm-to-mm-scale nodules and Ca-sulfate veins [8].

Nontron and Bardou were analyzed over three nights in CheMin, for a total of 22.5 hours of integration. Nontron was analyzed in a Mylar cell, whereas Bardou was analyzed in a Kapton cell. Maria Gordon, Pontours, and Zechstein were each analyzed in a Kapton cell for a single night (i.e., 7.5 hours of integration on each sample).

Mineral Assemblages: The five samples drilled thus far from the clay-sulfate transition all have abundant plagioclase and amorphous materials, minor to trace amounts of pyroxene, trace quartz, and all but Zechstein have trace K-feldspar (Figure). The five samples, however, differ significantly in their secondary mineralogy:

Phyllosilicate. Nontron, which is the sample drilled closest to Glen Torridon, has the most phyllosilicate of the five samples, with 18 wt.% nontronite. Bardou contains 12 wt.% nontronite, Pontours and Maria Gordon have a trace amount of phyllosilicate, and Zechstein does not contain phyllosilicate above the CheMin detection limits of ~1 wt.% [e.g., 9].

Sulfate. Ca sulfate is the only crystalline sulfate detected by CheMin in the five clay-sulfate transition samples. All five samples have minor amounts bassanite ($CaSO_4 \bullet 0.5\ H_2O$). Nontron, Bardou, and Maria Gordon have trace to minor amounts of anhydrite ($CaSO_4$), whereas Pontours and Zechstein lack anhydrite. Bardou, Pontours, and Maria Gordon have trace gypsum, Nontron lacks gypsum, and Zechstein has abundant (~25 wt.%) gypsum. The high gypsum abundance in the Zechstein drill powder without elevated Ca and SO_3 in the pre-drilled surface suggests CheMin sampled a portion of a Ca-sulfate vein at depth. CheMin has not detected any crystalline Mg sulfate in the five samples.

Oxides/Oxyhydroxides. Hematite (α-Fe_2O_3) is present in all five samples in abundances of ~4 to ~8 wt.%, where Bardou has the most hematite and Pontours has the least. Trace amounts of goethite (α-FeOOH) are present in Nontron, Pontours, and Maria Gordon.

Carbonates and Halides. Trace amounts of ankerite ($Ca(Fe^{2+},Mg)(CO_3)_2$) are present in Nontron and Bardou. A trace amount of halite (NaCl) was detected in Pontours.

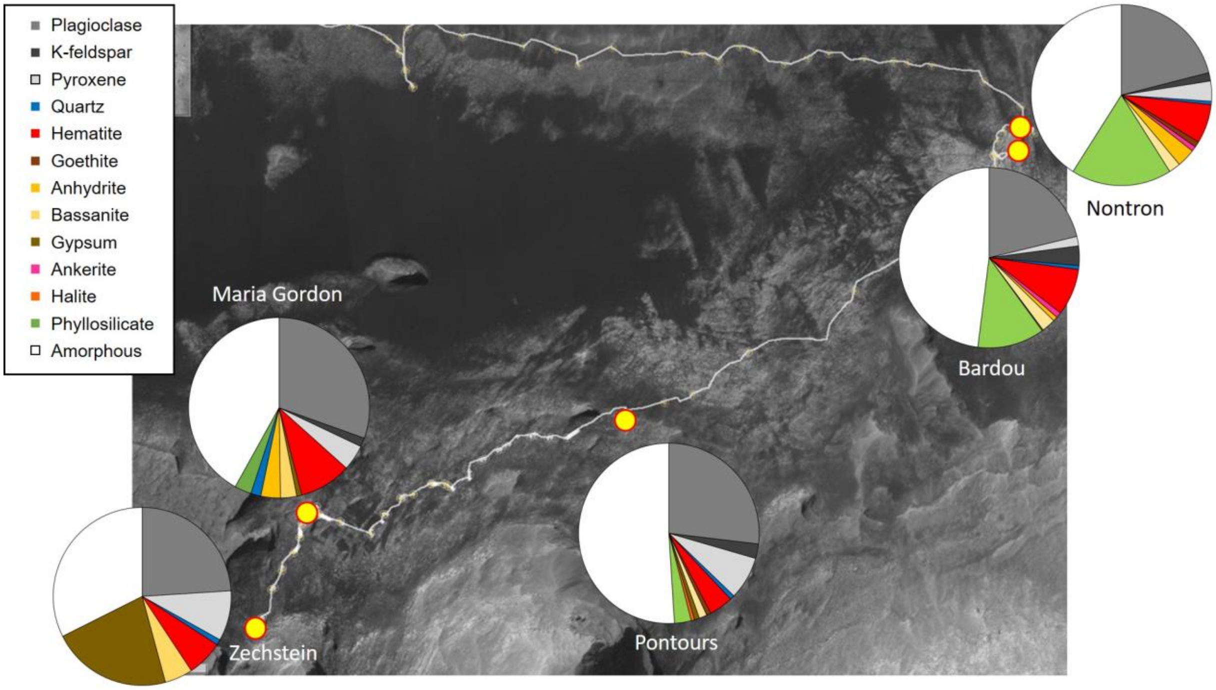

Figure. Mineral and amorphous abundances for the five drilled samples analyzed by CheMin in the clay-sulfate transition. The white line shows *Curiosity's* traverse, and yellow dots represent drill locations.

Mineralogical Trends over the Clay-Sulfate Transition: The five samples drilled in the clay-sulfate transition show important mineralogical trends with elevation that suggest changes in aqueous environments occurred between Glen Torridon and the rover's current location. The most obvious trend is the loss of phyllosilicate. CheMin data demonstrate a dramatic change in phyllosilicate abundances over ~100 m of stratigraphy, from ~30 wt.% smectite in Glen Torridon [5] to no phyllosilicate in Zechstein. This loss of phyllosilicate is coupled with a loss of Fe^{2+}-bearing carbonate. The clay-sulfate transition has significantly more hematite than Glen Torridon, and trace goethite has been identified by CheMin for the first time in the mission.

Mineralogical differences between the smectite-rich Glen Torridon and the stratigraphically equivalent hematite-rich Vera Rubin ridge may have resulted from saline, silica-poor groundwater destabilizing phyllosilicates and causing the precipitation of hematite on the ridge [10]. The loss of both phyllosilicate and carbonate over the clay-sulfate transition is consistent with this hypothesis and suggests groundwater with low alkalinity and low $SiO_{2(aq)}$ interacted with these sediments to remove these phases. Alternatively, fluids may have evolved to low alkalinity and low silica over time such that phyllosilicate and carbonate precipitation became unfavorable. Goethite dehydrates to form hematite with burial [e.g., 11], so the discovery of trace goethite with hematite may signify a lower degree of burial diagenesis in the clay-sulfate transition.

Compositional data from *Curiosity* support salty diagenetic fluids in the clay-sulfate transition. Trace halite in Pontours indicates sporadic saline fluids in this interval. Although CheMin has not detected crystalline Mg sulfates so far, SAM data identified Mg sulfate in Pontours, Maria Gordon, and Zechstein, indicating Mg sulfate in these targets is X-ray amorphous [12]. Furthermore, geochemical data from ChemCam and APXS show nodules are enriched in sulfur, demonstrating sulfates are likely diagenetic products that are heterogeneously distributed in the bedrock.

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