FACTORS INFLUENCING THE FORMATION AND ABUNDANCE OF X-RAY AMORPHOUS MATERIALS DETECTED IN GALE CRATER MUDSTONES AND SANDSTONES.

C. N. Achilles[1], E. B. Rampe[2], T. S. J. Gabriel[3], D. W. Ming[2], R. V. Morris[2], B. Sutter[4], S. J. Chipera[5], D. F. Blake[6], T. F. Bristow[6], R. T. Downs[7], A. C. McAdam[1], L. Thompson[8], D. T. Vaniman[9], A. S. Yen[10], [1]NASA GSFC (cherie.n.achilles@nasa.gov), [2]NASA JSC, [3]Arizona State Univ., [4]Jacobs Technology/NASA JSC, [5]Chesapeake Energy, [6]NASA Ames, [7]Univ. of Arizona, [8]Univ. of New Brunswick, , [9]Planetary Science Institute, [10]JPL/Caltech.

Introduction: The CheMin X-ray diffraction instrument on the Mars Science Laboratory rover has analyzed 22 mudstone and sandstone samples while exploring the layered sediments in Gale crater, Mars. CheMin data allow for the identification of crystalline phases with a detection limit of ~1 wt% and provide information regarding the relative abundance of well-crystalline, clay mineral, and X-ray amorphous materials [1,2]. Mineralogical assessments of Gale crater mudstones and sandstones are critical for evaluating detrital sources, lacustrine depositional environments, and the aqueous diagenetic history of analyzed samples [3-10]. On average, ~40 wt% of CheMin-analyzed rocks are composed of X-ray amorphous materials. The factors driving the formation of the X-ray amorphous component are poorly understood and may vary between each sample analyzed by *Curiosity*. Here, we examine 19 sandstone and mudstone samples analyzed by CheMin to assess the primary factors that influence the formation and abundance of X-ray amorphous phases identified in Gale crater rocks.

X-ray Amorphous Abundance and Composition: The chemical composition of the amorphous component is estimated from mass-balance calculations using the APXS-determined bulk composition of each sample and the quantity and composition of the crystalline components determined from Rietveld refinements of CheMin diffraction patterns. The minimum amorphous abundance, equal to the value resulting in a zero-oxide value in the mass-balance calculation, was used for each sample. Three rock groups are presented, 1) Bradbury group mudstones and sandstone [3,4], 2) Stimson formation sandstones [7], and 3) Murray formation mudstones and sandstone [5,8-10]. Gale soils [11-13] are shown for comparison with the rocks.

Controls on Amorphous Phase Formation:

Silicate Alteration: The alteration of silicates correlates to an increase in the amorphous fraction (Fig. 1). Primary silicates (i.e., olivine, pyroxene, feldspar) alter to secondary crystalline minerals (e.g., phyllosilicates, magnetite), and/or X-ray amorphous materials. If all alteration products were crystalline, the amorphous fraction would remain unchanged from the parent material or would decrease if volcanic glass were altered to phyllosilicate. However, the negative correlation shown in Fig. 1 suggests that as silicate alteration increases more X-ray amorphous materials are produced relative to crystalline materials. The depositional and diagenetic history of the rocks also affects the observed trend. Bounding the range in amorphous abundance are samples drilled from the Stimson fm. sandstones. The mineralogy of parent sandstones (BS and OK) suggest minimal aqueous alteration, whereas the GH and LB samples drilled from alteration halos show a substantial loss of parent crystalline materials and >3x increase in the X-ray amorphous fraction [7]. The alteration history proposed for GH and LB involves multiple aqueous alteration stages, low water-to-rock ratios, and exposure to low and moderate pH fluids [7]. Although evidence for diagenesis exists in all rocks drilled by *Curiosity*, Stimson fm. alteration halos are extensively leached and one of the most intensely altered rocks observed at Gale crater. Multiple alteration events are proposed for Bradbury gr. and Murry fm. mudstones and sandstones [3,5,9], however compared to Stimson fm. rocks, substantial variation in the depositional and diagenetic conditions (e.g., water-to-rock, pH) strongly influenced the extent to which silicates altered and X-ray amorphous materials formed.

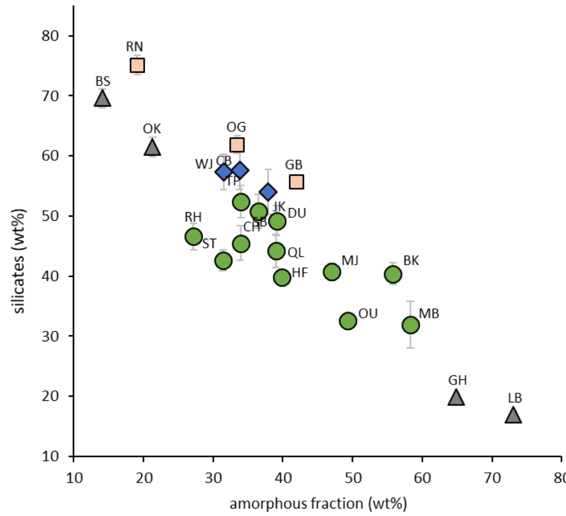

Figure 1. Silicates (including phyllosilicates) vs. the calculated minimum amorphous abundance. Soils (tan squares; RN=Rocknest, GB=Gobabeb, OG=Ogunquit Beach), Bradbury gr. (blue diamonds; JK=John Klein, CB=Cumberland, WJ= Windjana), Stimson fm. (grey triangles; BS=Big Sky, OK= Okoruso, GH=Greenhorn, LB=Lubango), and Murray fm. (green circles, CH=Confidence Hills, MJ=Mojave, TP=Telegraph Peak, BK=Buckskin, OU=Oudam, MB=Marimba, QL=Quela, SB= Sebina, DU=Duluth, ST=Stoer, HF= Highfield, RH=Rock Hall)

Clay Mineral Formation: Among clay-bearing samples in Gale crater, a positive trend between clay mineral and amorphous fraction abundance is observed

(Fig. 2, clay formation arrow). Ideal hydrolysis reactions of olivine, pyroxene, and feldspar to smectite result in the incorporation of Si within the clay mineral structure and minor leaching of Mg^{2+}, Fe^{2+}, Ca^{2+}, and Na^{+} ions to the solution. Some ions, like Fe^{2+} and Fe^{3+}, can form secondary crystalline phases, like the magnetite observed in some mudstones [3,5]. Amorphous Fe-oxides, amorphous Mg- and Fe-sulfates, and poorly crystalline residues may also result from silicate alteration to clay minerals. Ideally, these short-order materials develop into more stable forms (i.e. crystalline structures); however, the increase in the amorphous:crystalline ratio suggests that conditions promoting equilibration (e.g., temperature, time) were insufficient and resulted in some products to persist in an amorphous state.

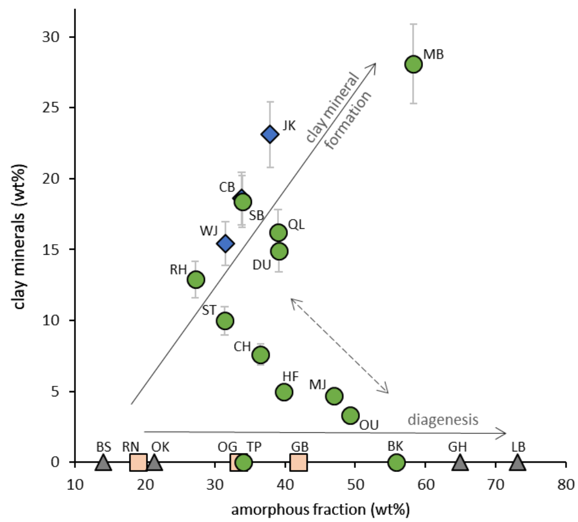

Figure 2. Clay mineral abundance vs. the calculated minimum amorphous abundance. See Fig. 1 caption for legend.

Rock samples CH, HF, MJ, and OU do not follow the trend described above. Two factors contribute to this diversion: depositional environment and post-depositional alteration. Conditions supporting clay mineral formation in other Gale samples may have been absent or restricted during deposition of CH, HF, MJ, OU and non-clay mineral bearing muds (TP, BK), depressing clay mineral reaction kinetics. The reduced potential for clay mineral formation would also reduce the X-ray amorphous materials associated with the dissolution reactions. The increased amorphous fraction must result from subsequent silicate alteration events. HF and OU exhibit mineralogical evidence of hydrothermal alteration [9,10]. A high abundance of jarosite in MJ records an intense fluid event marked by low pH [5] and the adjacent CH may have, to a lesser extent, been altered by the same acidic event. The result is a mixing line between clay mineral formation and post-depositional alteration processes (Fig. 2, dashed arrow).

Amorphous SiO_2: The processes that cause amorphous silica to correlate with amorphous concentration likely differ among clay mineral bearing and non-clay mineral bearing samples (Fig. 3). For example, incomplete silicate-to-smectite reactions may contribute Si-rich residues in clay mineral bearing samples. In both clay-bearing and non-clay bearing samples, passive silica enrichment can result from acidic leaching events by removal of metal cations following mineral dissolution (e.g., GH, LB) [7]. The highest amorphous SiO_2 abundances are observed in the GH, LB, BK. These samples are tightly clustered, a possible indication that the alteration history of the sandstones and mudstone are related. Chemical evidence for hydrothermal and/or acidic alteration in the BK mudstone maybe related to the same fluid event(s) that produced the alteration halos in the Stimson sandstone [14].

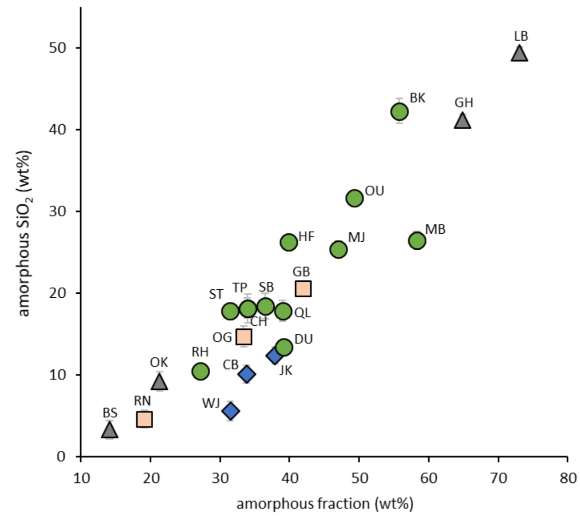

Figure 3. Amorphous SiO_2 vs. the calculated minimum amorphous abundance. See Fig. 1 caption for legend.

Conclusions: Three factors contribute to amorphous material formation in Gale crater: 1) the degree of silicate dissolution, 2) clay mineral formation, and 3) fluid conditions (i.e., water-to-rock, pH, time). Water-to-rock ratio is one of the most influential factors impacting both clay mineral and non-clay mineral bearing rocks. The correlation between amorphous and clay mineral abundances may signify low water-to-rock ratios promoting non-ideal or incomplete reactions resulting in silica-rich amorphous residues. In both clay mineral and non-clay mineral bearing rocks, multiple alteration episodes with a low water-to-rock ratios can cause ion mobilization and passively enrich Si. Further characterizing martian amorphous materials is critical to understanding Mars' aqueous history through time.

References: [1] Blake et al., 2012. [2] Chipera and Bish, 2013. [3] Vaniman et al., 2013. [4] Treiman et al., 2016. [5] Rampe et al., 2017 [6] Hurowitz et al., 2017. [7] Yen et. al., 2017. [8] Bristow et al., 2018, [9] Achilles et al., submitted [10] Rampe et al., submitted [11] Blake et al., 2013, [12] Achilles et al., 2018, [13] Rampe et al., 2018. Yen et al., submitted.