FACTORS INFLUENCING THE FORMATION AND PRESERVATION OF X-RAY AMORPHOUS MATERIALS IDENTIFIED IN SEDIMENTARY DEPOSITS AT GALE CRATER, MARS

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Introduction: The CheMin X-ray diffraction instrument on the Mars Science Laboratory (MSL) rover has analyzed three sediments and 27 sedimentary rocks 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 mineral, clay mineral, and X-ray amorphous materials [1,2]. The mineralogy of Gale crater samples is critical for evaluating detrital sources, depositional environments, and diagenetic processes [3-10]. On average, ~40 wt% of CheMin-analyzed rocks are composed of X-ray amorphous materials. Amorphous materials are primary constituents of the parent rock or secondary products of weathering. Primary amorphous phases are mainly glasses with pyrogenic origins (e.g., volcanism and impacts). Chemical alteration of primary glasses and volcanic minerals result in both crystalline and amorphous secondary phases. Typically, on Earth, olivine, pyroxene, plagioclase, and glass alter to clay minerals and Fe-oxides/hydroxides [e.g., 11-13]. The partial and/or incomplete alteration of silicates may result in the formation of amorphous silica-rich gels or other mixed-cation residues [e.g., 12,14,15]. Multiple alteration episodes can increase the diversity of alteration products formed; however, the association between the quantity and chemical composition of the amorphous component, and the alteration history of the sedimentary deposits is poorly understood.

X-ray Amorphous Abundance and Composition: Bulk sample analyses of sedimentary deposits are performed by three MSL instruments: APXS (Alpha Particle X-ray Spectrometer), CheMin, and SAM (Sample Analysis at Mars). 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. SAM evolved gas data also provide information regarding volatile-containing crystalline and amorphous materials (e.g., phyllosilicates, amorphous sulfates, etc.; 16). Here we calculate the amorphous composition by subtracting the crystalline oxide composition (from CheMin analyses) from the bulk composition (from APXS) to determine the amorphous composition. We present data from three sediments [17-20] and three sedimentary rock groups: 1) Bradbury gp. mudstones and sandstone [3,4], 2) Siccar Point gp. sandstones [7], and 3) Mount Sharp gp. mudstones and sandstones [5, 8-10].

Amorphous Phase Formation and Preservation: Detrital materials and aqueous alteration conditions are the primary factors dictating the magnitude and composition of the amorphous fraction in Gale crater samples. Amorphous chemistries point to key factors contributing to the observed assemblages in Gale crater rocks. Most apparent are positive correlations between the fraction of SiO_2 and FeOT attributed to the amorphous component and the amorphous abundance (Fig. 1). These trends suggest that Si- and Fe-bearing amorphous products (i.e., Si-bearing residues, opaline silica, and amorphous Fe-oxides; 12-14) are common products of alteration. Some conditions can augment the amorphous fraction: low-pH can enhance mineral dissolution, low water-to-rock ratios can kinetically inhibit dissolution/precipitation reactions, and/or brief fluid exposure can cause reactions to cease prior to completion. Conversely, some alteration processes are conducive to crystallization (e.g., maturation by warm fluids, etc.) and the fraction of amorphous SiO_2 and FeOT will decrease if rocks are exposed to such conditions (e.g., 23). Figure 1 depicts data for all Gale crater sedimentary deposits and are discussed in detail below.

Gale Crater Sediments: The chemistry and mineralogy of CheMin-analyzed Gale crater soils indicate different source rocks and mineral variations attributed to physical sorting processes [18,19]. Two sediments have elevated SiO_2 and, of the SiO_2 detected, a higher fraction is attributed to the amorphous component (Fig. 1a). Basaltic glass is inferred to be a significant component of these SiO_2-rich sediments, whereas a glass-poor basalt is likely the source of the SiO_2-poor sediment [21]. This range in amorphous composition and glass content signifies diversity among basaltic detritus transported to the Gale crater basin.

Gale Crater Sedimentary Rocks: The wide range of amorphous magnitudes in Gale crater rocks suggest diverse detrital sources and varying degrees of alteration. For a subset of rocks, the mineralogy and chemistry suggest extensive, late-stage diagenesis; however, most rocks possess assemblages reflecting minimal to moderate alteration during early-stage diagenesis (i.e., deposition, authigenesis).

Among the three rock groups investigated, Siccar Point group sandstones include both the most crystalline- and amorphous-rich rocks observed in Gale crater (Fig. 1, gray diamonds). The mineralogy of the least-
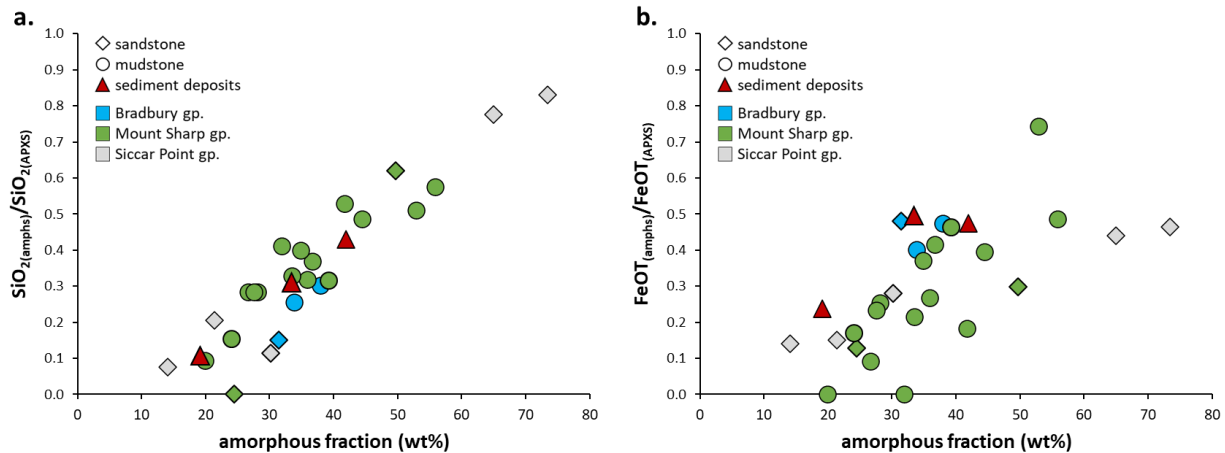
Figure 1. The fraction of total SiO$_2$ (a) and FeOT (b) attributed to the amorphous component versus the calculated, minimum amorphous abundance for all CheMin-analyzed Gale crater samples.

altered sandstone reflects an alteration history dominantly influenced by pore water-basalt interactions during diagenesis [7]. The two samples with a high fraction of SiO$_2$ in the amorphous component exhibit a substantial loss of primary minerals, generating a more than 3-fold increase in the total amorphous fraction and amorphous silica (Fig. 1a; 7). Multiple alteration episodes or a single event with evolving fluid properties facilitated the removal of cations by acidic leaching, and both passively and actively enriched SiO$_2$ [e.g., 7,22,23]. These rocks demonstrate the strong correlation between the number, duration, and/or intensity of alteration events and a net increase in the quantity and silicic nature of the amorphous fraction.

Intermediate to the Siccar Point group rocks are twenty Bradbury and Mount Sharp group mudstones and sandstones with amorphous components reflecting diverse geologic histories. Although no Bradbury or Mount Sharp group rocks exhibit amorphous composition extremes like those in the Siccar Point group, some phyllosilicate-rich rocks (e.g., Glen Torridon unit) have low amorphous SiO$_2$ fractions, uncharacteristic of the moderate amorphous SiO$_2$ abundances observed in all other clay mineral-rich rocks. This contradiction may suggest a phyllosilicate-bearing detrital source and minimal alteration upon deposition or, clay mineral formation in Fe-rich fluids whereby aqueous silica was consumed as phyllosilicates precipitated [24].

Conclusions: The amorphous component identified in Gale crater sedimentary deposits demonstrate diverse detrital sources and alteration histories. Sediments possess mineral and amorphous fractions most similar to unaltered basaltic rocks, but their amorphous compositions and magnitudes point to diverse detrital sources. Most mudstones and sandstones preserve amorphous assemblages generated in early-stage diagenesis. Intense, late-stage diagenesis is evident in rocks with abundant, and SiO$_2$-rich amorphous fractions. Amorphous chemistry trends suggest the degree of chemical

alteration controls the fraction of amorphous silica in Gale crater samples. Together, amorphous SiO$_2$ and FeOT fractions can facilitate the discrimination between minimal and more extensive alteration events and dominant fluid properties. By identifying these trends, the amorphous composition can uniquely characterize alteration conditions that cannot be derived from mineralogy or bulk chemistry alone.

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., 2020 [10] Rampe et al., 2020 [11] Eggleton et al. 1987 [12] Delvigne et al., 1979 [13] Delvigne et al. 1990 [14] Wilson, 2004 [15] Rampe et al., 2017 [16] Sutter et al. 2017 [17] Blake et al., 2013 [18] Achilles et al., 2018 [19] Rampe et al., 2018 [20] Bish et al., 2013 [21] Achilles et al., in prep [22] Frydenyang et al., 2017 [23] Gabriel et al. in review [24] Bristow et al. submitted