
Introduction: X-ray amorphous material has been detected by the CheMin X-ray diffractometer (XRD) in each of the 39 drill samples and 3 soil samples collected by the Curiosity rover to date [1-4]. The term ‘amorphous’ describes any phase that lacks long-range atomic order; here we use the term ‘X-ray amorphous materials’ to include nanocrystalline phases that scatter X-rays (i.e., they may contain short-range atomic order below the resolution of the XRD). This X-ray amorphous component is a major constituent (~20-75 wt %) of rock and soil samples in Gale crater, indicated by a characteristic hump in the X-ray diffraction patterns, the location of which can be diagnostic of different types of amorphous material (e.g., for amorphous glassy phases the center of this hump is located between ~25 and 30° 20) [1-4]. The origin(s) of these materials remains speculative; naturally occurring amorphous materials are found in a variety of environments and can be primary (e.g., volcanic or impact-produced glasses and spring deposits) or secondary (e.g., aqueous alteration) products. In Gale crater, the X-ray amorphous component could consist of primary glass(es) deposited in elolian, fluvial, or lacustrine environments or secondary products precipitated during diagenesis [1-10]; it is likely to be a mixture of these.

As Curiosity left the Fe/Mg phyllosilicate-rich Glen Torrion region, traversed across the clay-sulfate transition and arrived at the sulfate unit, several noteworthy mineralogical trends were observed, many of which were also predicted and validated against premission remote sensing datasets. One of the most distinct of these changes was the loss of phyllosilicates through the transition from older Fe/Mg smectite-rich sandstones and mudstones in Glen Torrion to the younger, phyllosilicate-barren, hydrated Mg-sulfate-rich (+/- Fe(II) carbonate) sandstones [10,11]. These temporal changes in mineralogy and geochemistry can be traced across the planet and are thought to represent a change from a warm and wet to cold and dry climate [12,13]. Throughout these dramatic paleoenvironmental changes observed in the sedimentary rocks of Gale crater, the abundant X-ray amorphous component has persisted in every drilled sample.

In this contribution, we present major trends in the abundance and composition of the X-ray amorphous component across this region of major change, through the Fe/Mg phyllosilicate-rich strata, clay-sulfate transition and sulfate unit, and place these data within the context of the observed mineralogical trends. We also discuss potential origin(s) of the X-ray amorphous material and paleoenvironmental indicators.

Methods: The elemental composition of the amorphous component is determined using a mass balance calculation, in which the elemental composition of the crystalline component (determined from CheMin XRD Rietveld refinements) [14] is subtracted from the overall elemental composition of the sample (determined from the Alpha Particle X-ray Spectrometer (APXS) analysis [2, 4, 6, 15]). APXS post-sieve dump pile analyses were used when available, to be most consistent with the CheMin analyses; when these were not available, analyses of the drill bit tailings were used. Phyllosilicates, when detected, were included in the crystalline component; their abundances and types were estimated using a combination of FULLPAT and Sample Analysis at Mars (SAM) datasets. The abundance of amorphous material was separately determined using FULLPAT. For several samples the amorphous component was underestimated by FULLPAT, yielding unrealistic (e.g., negative) oxide abundances. In these cases, the amorphous component was increased until a realistic (non-negative) composition was reached. This method is not without uncertainties and assumptions (e.g., ideal crystal chemistry for some minerals) but it provides a rough estimate to examine overall trends in the composition of the amorphous component, which when combined with other instrument datasets can help shed light on the regional trends and origin of the amorphous component across all drilled units in Gale crater.

Results and Discussion: Trends in the abundance of the amorphous component: The relative abundance of the amorphous component, when compared with the crystalline component (including clay minerals) has gradually increased along the traverse through the phyllosilicate-rich strata (average ~40 wt%), clay-sulfate transition (average ~55 wt%) and into the sulfate unit (average ~61 wt%) (Fig. 1). The highest
abundance observed to date is in sample Zechstein (ZE) (~75 wt%); however, it should be noted that this particular drill sample likely contained a localized diagenetic vein and therefore is not representative of the host unit. This increase in amorphous abundance also coincides with the observed absence of phyllosilicates, which have not been detected beyond the clay-sulfate transition in the sample Pontours (PT).

Trends in the elemental composition of the amorphous component: The amorphous material is primarily composed of the major oxides SiO₂, FeO₇, MgO and SO₃; other oxides are present but often comprise less than ~3 wt % of the sample or possess substantial errors. One of the most notable trends in amorphous material composition is the relationship between SiO₂ and SO₃, which suggests there are likely at least two major amorphous endmembers: one that contains abundant silicate and one that is more sulfate-rich. This relationship may reflect complex mixtures of primary and secondary materials. For example, primary impact and volcanic glasses would have an aluminosilicate composition, and amorphous sulfates with similar composition to the crystalline sulfates recently detected by CheMin (e.g., hydrated Mg-sulfate [11]) could comprise the amorphous sulfate endmember. The amorphous aluminosilicate endmember could also contain x-ray amorphous clay minerals, represent destroyed clay mineral components or clay mineral precursors (e.g., palagonitic material, allophane). Fig. 2 shows the relationship of SiO₂ and SO₃; using these datasets we will model hypothetical amorphous sulfate compositions (e.g., SO₃ + MgO + FeO₇) and aluminosilicate endmembers (e.g., SiO₂ + Al₂O₃).

There is also a gradual increase in amorphous FeO₇ across the clay sulfate transition (FeO₇ = ~20.3 +/- 1.5 wt%; normalized to 100 wt%) and sulfate units (~21.3 +/- 1.5 wt%; normalized to 100 wt%) compared to the Glen Torridon region (~16.4 +/- 2.8 wt%; normalized to 100 wt%). Experimental work that may help shed light on Mars-relevant amorphous sulfates is ongoing [16]. The amorphous component within the first drill sample marking the sulfate unit boundary, Canaima (CA), contained the highest abundance of MgO to date, ~14.6 +/- 3.7 wt% (normalized to 100 wt%); this is also the first drill site where the mineral starkeyite (MgSO₄·4H₂O) was detected [11]. This trend does not continue in the next sample analyzed, Tapo Caparo (TC), which contained ~7.1 +/- 0.5 wt% MgO.

Figure 1: Distribution of crystalline (including clays) and x-ray amorphous components from drill holes Aberlady (AL; bottom), in the Fe/Mg-smectite rich Glen Torridon region, through Tapo Caparo (TC; top), in the sulfate unit.

Figure 2: The composition of X-ray amorphous material, identifying SO₃ and SiO₂-rich amorphous phases; these data are not normalized to 100 wt % and obtained from the Fe/Mg-smectite rich Glen Torridon region (AB; Aberlady) through the sulfate unit (TC; Tapo Caparo).