BULK COMPOSITIONS OF X-RAY AMORPHOUS MATERIALS IN SOILS AND SEDIMENTS ON EARTH COMPARED TO X-RAY AMORPHOUS MATERIALS IN GALE CRATER, MARS.

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Introduction: The Curiosity rover has investigated several hundred stratigraphic meters of fluviolacustrine sedimentary rocks in Gale crater, Mars [1-2]. All of the samples measured by the CheMin X-ray diffractometer (XRD) instrument contain high abundances (~15-60 wt.%) of an X-ray amorphous component (AmC) of unknown origin [3-12]. The bulk compositions of the AmCs are inconsistent with a single known X-ray amorphous material (*e.g.*, basaltic glass, ferrihydrite), indicating that the AmCs contain multiple phases [6, 13]. Hypotheses for the origin of these materials include: (1) weathered basaltic glass [3, 9], (2) detrital and subsequently altered soil or aeolian material [5-6], or (3) diagenetic cement [8].

X-ray amorphous weathering products are frequently found in relatively young soils and sediments on Earth [*e.g.*, 14-16], and have been found in 20-60 Ma paleosols [17]. The AmC compositions of terrestrial samples could help determine the significance of martian AmCs. Unfortunately, very few terrestrial samples have been studied using the mass balance calculation (MBC) approach that is applied to samples in Gale crater [17-18], so it is not certain how bulk AmC compositions change with formation environment or are preserved through geologic time.

Here we apply the MBC approach to a diverse suite of terrestrial samples in order to determine how formation environment, climate, and diagenesis affect the composition of bulk AmCs. Terrestrial AmC compositions are then compared to AmC compositions calculated for samples in Gale crater.

Methods: Our sample suite includes sediments from recently de-glaciated basaltic to basaltic andesite volcanoes [19], modern basaltic volcanic soils from Hawaii [20], and basaltic andesite volcanic paleosols [21]. The MBC method combines bulk XRD mineralogy with bulk elemental analyses to calculate the bulk AmC composition. Mineral abundances are derived from Rietveld refinements of XRD patterns measured on a Panalytical instrument with a Co-Kα source. Elemental chemistry is measured via XRF, titration (FeO), IR (S), and INAA (Cl).

Soil and sediment samples were sieved to <150 μm to be consistent with CheMin measurements, and paleosols were crushed to ~sand-sized particulates. XRD powders were prepared in a micronizing mill with internal standards (20 wt.% Al_2O_3) to quantify crystalline phases and the AmC.

It is important to note a few limitations of the MBC method. First, the composition of crystalline phases that are below the detection limit of XRD will be allocated to the AmC composition. Second, minor elemental substitutions not reported in the ideal structure formula for crystalline minerals are also allocated to the AmC composition. Third, clay minerals can have complex compositions, and when poorly constrained, their presence makes it difficult to precisely determine the AmC compositions [6].

Results: *Terrestrial AmC compositions.* Preliminary results suggest that the AmCs of terrestrial samples consist primarily of SiO_2, Al_2O_3, TiO_2, FeO_{Total}, with lesser amounts of other oxides (*e.g.*, MgO, CaO, Na_2O; Fig. 1a). None of the bulk AmCs are consistent with a single known X-ray amorphous material, indicating multi-phase mixtures. Compared to their respective crystalline counterparts, the glacial samples have bulk AmCs enriched in SiO_2 and FeO_{Total}, and depleted in Al_2O_3. In contrast, the AmCs of the modern soil and paleosol samples are mostly depleted in SiO_2 compared to their crystalline counterparts (Fig. 2a).

Martian AmC compositions. The AmCs of martian samples consist primarily of SiO_2, SO_3, FeO_{Total}, with highly variable amounts of other oxides (*e.g.*, Al_2O_3, MgO, CaO, Na_2O; Fig. 1b). There are distinct trends in major oxide ratios for the AmCs of different stratigraphic units in Gale crater. The AmCs of the Bradbury group rocks tend to be enriched in FeO_{Total} when compared to their crystalline counterparts (Fig. 2b,
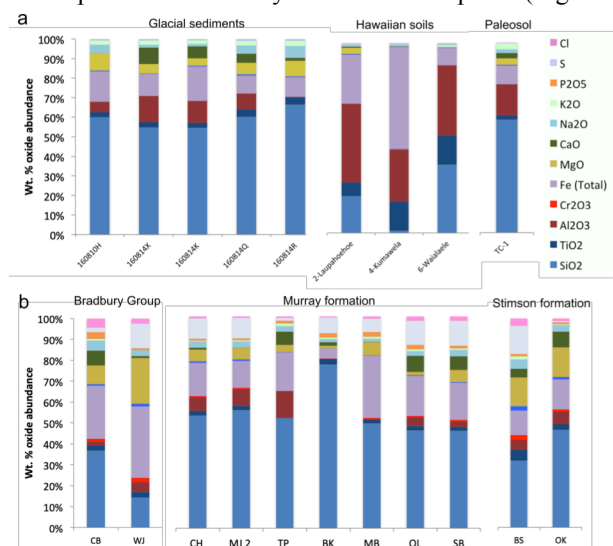
Figure 1. Bulk AmC compositions of (a) terrestrial samples compared to (b) martian samples [6, 8-12].
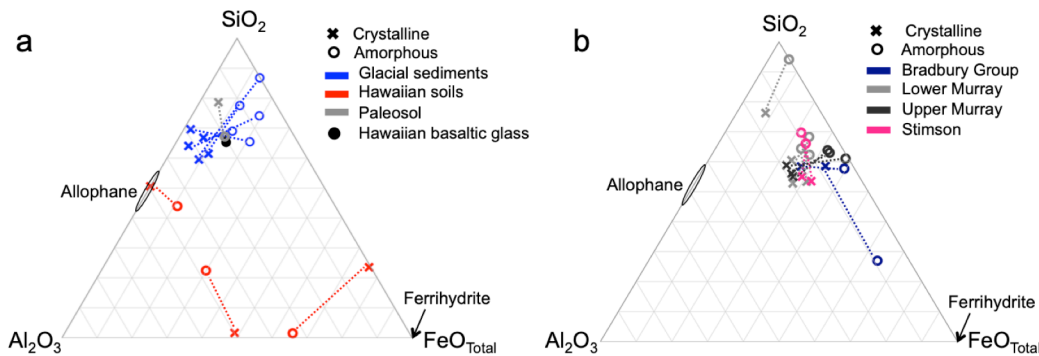
Figure 2. Major oxide ratios in weight % for bulk X-ray amorphous and crystalline component compositions derived using the MBC method for (a) terrestrial soils, sediments, and paleosols and (b) martian sediments and sedimentary rocks [6, 8-12].

blue markers). Whereas, Stimson formation rocks have AmCs that are relatively enriched in SiO_2 compared to their crystalline counterparts (Fig. 2b, pink markers). Preliminary MCB results for upper Murray rocks (MB, QL, SB; [12]) suggest that their AmCs are more enriched in FeO_{Total} and less enriched in SiO_2 (Fig. 2b, black markers) than the AmCs in rocks in the lower Murray formation (CH, MJ, BK, TP), which are enriched in SiO_2 when compared to their crystalline counterparts (Fig. 2b, grey markers).

Discussion: TEM analyses indicate that the AmCs in terrestrial samples are mostly weathering products. Therefore, our MBC results show that bulk AmC compositions do vary between weathering environments – in particular, the relative enrichment or depletion in SiO_2. SiO_2 is highly mobile during the weathering of mafic parent materials [22]. Yet, colder and more rapid weathering during melt events in glacial environments preferentially forms poorly crystalline phases that take up the SiO_2 in solution [23] (Fig. 2a, blue markers). In developed soils in warm and wet environments, most of the SiO_2 is removed from the system, but what is left is taken up by more crystalline minerals, like clays (Fig. 2a, red markers). Most of the bulk SiO_2 also ends up in crystalline clays, rather than the AmC, for the one paleosol studied thus far (Fig. 2a, grey marker).

Comparison to martian samples: The overall bulk AmC compositions of the Murray and Stimson martian rocks are most similar to the AmCs of our glacial and paleosol samples, with the exception of higher SO_3 and Cr_2O_3 in the martian samples (Fig. 1). The high SO_3 abundances in martian CH, MJ, and TP AmCs have been attributed to episodes of diagenesis [9], and a similar argument can be made for the other Murray samples (Fig. 1b). As observed in our terrestrial sample set, martian rocks with higher abundances of clay minerals (upper Murray; ~16-28 wt.%; [24]) exhibit lower SiO_2 in their AmCs than rocks with lower clay abundances (lower Murray; ~0-7.5 wt.%; [9]).

The Bradbury group samples exhibit markedly different bulk AmC compositions compared to our terres-

trial samples, with depleted SiO_2 along with low Al_2O_3 abundances and higher abundances of mono- and divalent cation oxides (*e.g.*, MgO, Na_2O) than any bulk or individual X-ray amorphous composition observed in our samples thus far.

Summary: The AmCs of both terrestrial and martian samples are multi-phase mixtures, containing iron oxides and (alumino)silicates, with an additional sulfate component in the martian samples. The components of these mixtures may have different origins. Sulfate AmCs in martian samples likely represent post-depositional diagenesis [9], while similarities between some terrestrial and martian iron oxide and aluminosilicate AmCs suggest that these components can be consistent with a detrital origin (*e.g.*, formed during weathering elsewhere and transported to Gale crater). Yet, a diagenetic origin for these materials cannot be ruled out since it is still unclear how detrital AmCs persist through diagenesis, and X-ray amorphous silicates and iron oxides are common cementing materials in terrestrial sedimentary rocks. Further analyses of our paleosols will help constrain the relative importance of weathering vs. diagenesis in the formation of martian X-ray amorphous components.

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