HIGH RESOLUTION IMAGING AND ANALYSIS OF TERRESTRIAL IMPACT GLASS: AMORPHOUS MATERIALS, PHYLLOSILICATES AND EVERYTHING IN BETWEEN. S. L. Simpson[1], E. B. Rampe[1], R. Christoffersen[2], L. P. Keller[1], R. Jakubek[2], V. Tu[2], D. A. Kring[3], F. J. Longstaffe[4], G. R. Osinski[4], [1]NASA Johnson Space Center, Houston, TX, 77058, USA (sarah.l.simpson@nasa.gov), [2]Jacobs at NASA Johnson Space Center, Houston, TX, USA, [3]Lunar and Planetary Institute, Houston TX, [4]Western University, London, Canada.

Introduction: Impact cratering is one of the most ubiquitous geologic processes shaping the surface of all solid bodies in our solar system. Impacts are also a major source of clay minerals, poorly crystalline clay-like phases and amorphous (i.e., lacking long-range atomic order) materials on Earth and Mars (e.g., [1-5]). Phyllosilicates and amorphous materials have consistently formed a major component (~20-70 wt%) of every single drilled rock and soil sample in Gale Crater on Mars, as determined by the CheMin instrument on *Curiosity* (e.g., [3, 6]). The origin of the amorphous component is speculative, but could be primary impact or volcanic-produced glass(es) deposited via aeolian or fluvial processes, secondary aqueous alteration products or chemical precipitates; it is likely to be a combination of all three possibilities. Efforts to determine the composition of these materials across the rover's traverse through Gale Crater are ongoing [6]. Naturally occurring amorphous phases are found in a variety of environments on Earth, and terrestrial analogue studies may help shed light on how they may have formed on Mars (e.g., [5,7]). Primary and altered impact glass are likely widespread on Mars and may have contributed to the amorphous component found throughout Gale Crater [1,4,8].

In its pristine, unaltered state, impact glass (i.e., melt glass) is considered amorphous. However, truly unaltered glass is rarely preserved in crater fill impactites as it quickly alters in the post-impact environment, commonly forming a mixture of hydrated aluminosilicate phases whose structures are not always discernable at the microscale (i.e., they may be amorphous or contain short-range order). These phases are part of an incredibly complex group of materials; differences in their composition and crystalline structure (or lack thereof) and genetic relationship to the more well-crystalline clay minerals are often only discernable at the nanoscale, beyond the resolution of traditional X-ray diffractometers (XRD) and scanning electron microscopes/microprobes (SEM/EPMA) alone. In this contribution, we summarize recent results from ongoing characterization of clay minerals, poorly crystalline clay-like phases, and amorphous materials preserved in altered terrestrial impact glass from the Chicxulub (~66 Ma) and Ries (~15 Ma) impact structures. This work has been performed using a combination of high-resolution transmission electron microscopy (HR-TEM), SEM, microprobe/EPMA, Raman spectroscopy and XRD.

Methods: Samples of impact melt-bearing breccia from the Chicxulub peak ring (Unit 2) were acquired during the 2016 joint IODP-ICDP Expedition 364 [9,10] and samples of melt-bearing impact breccia ("suevite") from the Aumühle quarry in the Ries crater, Germany were acquired by DAK during a previous field campaign. Petrographic thin sections were initially characterized using SEM and EPMA. Ultra-thin sections of altered glass clasts for TEM characterization were created using an FEI Quanta dual-beam focused ion beam (FIB) instrument and analyzed using a JEOL 2500SE field-emission scanning transmission electron microscope (FE-STEM). XRD data were obtained on (unoriented) bulk glass clasts using a Panalytical X'Pert Pro MPD. Single-point Raman spectra were collected on a WITec alpha300R Raman microscope using 488 nm excitation.

Results and Discussion: The first sample selected for FE-STEM analysis was a clast of altered glass from Chicxulub showing relict schlieren and possible melt immiscibility textures between two original end-member compositions. For simplicity, in this work two types of glass have been identified based on their color in transmitted light: green glass (GG) and brown glass (BG). Preliminary characterization in SEM and EPMA showed both types of altered glass are Mg-Fe rich, with varying amounts of water (~80 to 90 wt%), nanoscale crystallinity and textures that are distinct from coarser-crystalline phyllosilicates in the suevite [11]. *FE-STEM results*: HRTEM imaging in the JEOL FE-STEM instrument showed the altered glass from Chicxulub is made of three broad categories of material: (1) a phyllosilicate component with varying ~11.5 to 14.3 Å periodicity (Fig. 1) interpreted as the silicate sheet basal (001) spacing, (2) single, poorly formed sheet-like components, and (3) an amorphous component. FE-STEM EDS analysis indicates there are two distinct amorphous phases present: one is a carbon-rich vesicular phase and the other contains an aluminosilicate composition. Very little amorphous aluminosilicate was found in this sample; it could be primary impact glass, consistent with rare preservation in this environment. *Raman:* Spectra were obtained from both GG and BG and showed various secondary crystalline phases previously identified in SEM/EPMA and XRD, and also an amorphous carbon phase. The amorphous

carbon spectra contain G bands with a peak position of ~1595 to 1600 cm^{-1} and a full width at half height (FWHH) of ~35 to 40, whereas the D bands have a peak position of ~1350 to 1360 cm^{-1} and a FWHH of ~250 to 300 (Fig. 2). Spectra were also obtained on epoxy to exclude contamination. These band parameters suggest the amorphous carbon is a macromolecular carbon (MMC) that is highly disordered and has undergone little thermal maturation.

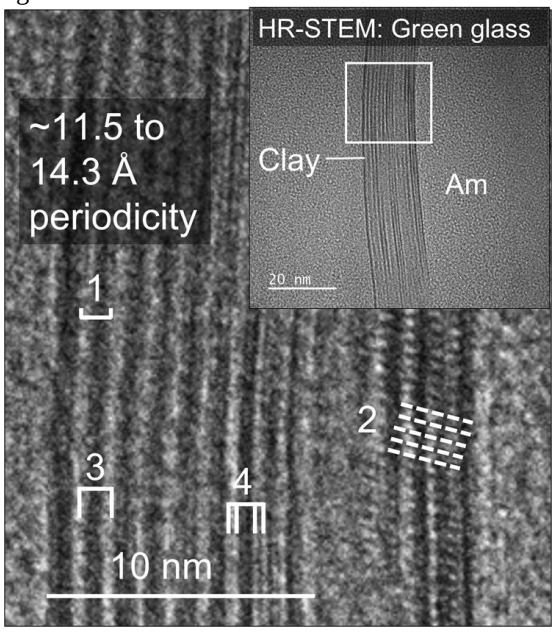

Figure 1: Transmission electron microscope images of a clay mineral with varying periodicity between ~11.5 to 14.3 Å (1), interpreted as the silicate layer basal (001) spacing. Area (2) denotes cross-fringe measurements interpreted as the clay mineral d(060), measuring ~1.50 to 1.53 Å. Sections (3) and (4) show some layer thickness variability. Am = amorphous.

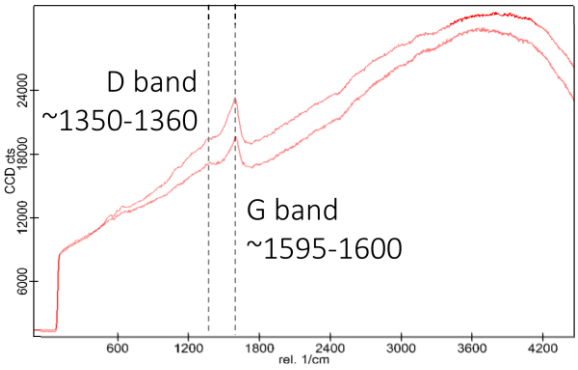

Figure 2: Raman spectra of amorphous macromolecular carbon (MMC) preserved in the Chicxulub impact glass.

Previous work focused on characterizing the clay mineralogy (<0.2 μm) of the Chicxulub upper peak ring breccias using pXRD indicated both tri- and dioctahedral smectites were the dominant phyllosilicate species [11]. One of the unusual, unresolved features noted in some of these samples was their resistance to collapsing "neatly" (i.e., from a 12.5 to 10 Å structure, typical of smectites) at 0% relative humidity (~107 °C) conditions. This was interpreted as the presence of weakly bound hydroxy-interlayered material, but the results presented here suggest those behaviors may also have arisen from the presence of weakly bound amorphous carbon [11]. The higher ~14.3 Å periodicities of these clays are consistent with chlorite, but chlorite was not identified via XRD (<0.2 μm size fraction), and the smectites should collapse to ~10 Å under vacuum, in TEM. The lower periodicities (~11.5 Å) may reflect the same behaviors observed in pXRD (Fig. 1), an inability to collapse due to weakly bound interlayer material. Amorphous carbon with spectral and textural features similar to those observed here have been noted in other terrestrial impact structures as well as ureilites [12-15]. It is unlikely that the Chicxulub glass-hosted MMC in this study is derived from an inorganic (carbonate) precursor, as the immediate post-impact environment precludes conditions required to reduce a carbonate to a hydrocarbon.

Combining Raman, XRD, and TEM here demonstrate an intimate mixture of phyllosilicates, poorly crystalline sheet-like silicates, and amorphous materials in impactites. We hypothesize similar materials will be present in surface samples collected by the *Perseverance* rover and delivered to Earth. These results also emphasize the potential role of impact cratering as a process in recycling/redistributing (or potentially destroying) organic carbon on the surface of ancient Mars, and whether amorphous MMC could be preserved in Martian impact glass. Moving forward, we will expand this work to samples with known carbonate melt phases and varying glass compositions (e.g., more well-preserved aluminosilicate glass, with varying water content) in the Ries impact crater. We will also continue to explore the origin and nature of the amorphous MMC preserved in the Chicxulub impact glass and its relationship with the clay minerals.

References: [1] Ehlmann et al., (2012) *Space Sci. Rev., 74,* 329-364. [2] Simpson, S. et al., (2022*) 53rd LPSC, #1549.* [3] Rampe, E. B. et al. (2020) *Geochem., 80,* 125605 [4] Smith, R., et al. (2021) *JGR Planets 126* [5] Thorpe et al. (2020) *51st LPSC, #1566*. [6] Simpson, S. et al., (2023) *this conference*, [7] Rampe, E. et al., (2022) *EPSL 584, 117471*. [8] Horgan, B. et al. (2022*) 85th Metsoc, #6526*. [9] Morgan, J. V. et al. (2016) *Science, 354,* 878–882. [10] Gulick, S. P. S. et al. (2018) *Proc. IODP Vol. 364*. [11] Simpson et al. (2022) *Chem. Geo.* 588. [12] Howard, K. et al., (2013) *Nature Geo. 6, 1018-1022*. [13] Shumilova, T. G., et al. (2018) *Sci. Rep., 8, 6923*. [14] Shumilova, T. G. et al., (2020) *IOP Conf. Ser.: Earth Environ. Sci. 609 012054*. [15] Le Guillou, C. et al., (2010) *GCA 74, 4167-4185.*