

AMORPHOUS PHASES ON THE SURFACE OF MARS. E. B. Rampe¹, R. V. Morris¹, S. W. Ruff², B. Horgan³, E. Dehouck⁴, C. N. Achilles⁵, D. W. Ming¹, D. L. Bish⁵, S. J. Chipera⁶, and The MSL Science Team, ¹NASA Johnson Space Center (elizabeth.b.rampe@nasa.gov), ²Arizona State University, ³Purdue University, ⁴Stony Brook University, ⁵Indiana University, ⁶CHK Energy.

Introduction: The importance of amorphous materials (including poorly crystalline and nanophase materials) on the surface of Mars has been recognized for decades. Amorphous phases have been detected through Earth-based and orbital IR spectroscopic observations, [e.g., 1,2], *in-situ* measurements by rovers and landers [e.g., 3,4], and laboratory studies of SNC meteorites [e.g., 5,6], and they have been predicted by geochemical modeling [e.g., 7]. Amorphous phases can form through primary (i.e., volcanism or impacts) or secondary processes (e.g., hydrothermal alteration, low-temperature weathering, radiation damage), and the types of amorphous materials present can tell us about past geologic and alteration processes. There are a variety of amorphous silicates that can be used to determine past aqueous environments, and here we focus on three key phases that have been detected on Mars. Opaline silica implies aqueous alteration at high water-to-rock ratios (leaching) under a range of temperature and pH conditions, including in marine deposits, hydrothermal systems, and soils [8]. Allophane (a poorly-crystalline aluminosilicate) implies low-temperature aqueous alteration at neutral to mildly acidic conditions, but only under rapid weathering that occurs in soils in snow-melt dominated climates and in young soils (especially glass-rich volcanic soils) in humid climates (>1 m mean annual precipitation) [9]. Finally, the presence of unaltered mafic glass can be used to infer a lack of aqueous alteration because it readily weathers in the presence of water.

Amorphous phases in geologic materials are difficult to study on Earth, let alone on Mars, because they are usually mixed with crystalline and/or other amorphous phases. Furthermore, amorphous phases lack long-range crystallographic order so that measurements that rely on crystal structure (e.g., X-ray diffraction) are non-unique, which can complicate a diagnostic identification. Despite these obstacles, we have made significant headway since the 2007 International Conference on Mars in understanding the amorphous materials on the martian surface. Here, we discuss orbital and *in-situ* detections of amorphous materials and their implications for processes on the martian surface, questions that still remain about amorphous phases on Mars, and potential paths toward answering those questions.

Orbital Detections: Regional-to-global-scale and local detections of amorphous phases have been made using thermal-IR (TIR) and visible/near-IR (VNIR)

datasets. Palagonite (i.e., altered volcanic glass) and amorphous iron oxides were suggested very early on as components of the martian surface based on VNIR reflectance data [1,10,11]. Amorphous silicate phases were modeled in Thermal Emission Spectrometer (TES) spectra of low-albedo regions across the planet and were initially identified as volcanic glass [12]. Subsequent models suggested that the high-silica phases could also be phyllosilicates, zeolites, or amorphous silica coatings [13-15]. Recent TES models and interpretations of OMEGA VNIR data indicate that altered volcanic glass may explain the high-silica phases detected in northern mid-to-high latitude regions, including Acidalia and Utopia Planitia. OMEGA spectra from these regions display a band near 1.15 μm and a concave upwards slope, analogous to lab VNIR spectra of Fe-bearing volcanic glasses that were leached under moderately acidic, arid conditions [16]. Similarly, models of TES data from northern Acidalia and Utopia Planitia identify allophane and high Si/Al gel, both of which form from the alteration of volcanic glass [17].

Localized hydrated silica deposits have been identified across the planet, including in finely stratified deposits in and around Valles Marineris [18], finely laminated deposits in western Hellas Basin [19], and within craters in the Nili Fossae region [20]. In all cases, the local mineralogy and morphology of these deposits suggest formation from aqueous alteration.

In-Situ Detections: Data from landed missions also indicate the presence of hydrated silica and altered glass on the martian surface. Opaline silica outcrops and soil (~65-92 wt.% SiO_2) were discovered by the Mars Exploration Rover, Spirit, adjacent to Home Plate [21]. These deposits may have formed by acid-sulfate leaching of basaltic precursor materials [21] or from near-neutral, silica-enriched solutions from hot springs and/or geysers [22]. Mini-TES models of Clovis and Watchtower class rocks in the Columbia Hills of Gusev crater detected basaltic glass in ~35-50 vol.% abundances [23]; however, the best-fit spectral endmember came from a natural glass from Hawaii that showed evidence for a secondary coating or rind, likely from alteration of the glassy surface by meteoric water acidified by vent gases, similar to the alteration proposed for the northern lowlands glass above [16]. Mineralogy calculated from APXS data from the Clovis and Watchtower class rocks indicates the presence of secondary aluminosilicates, including allophane and

amorphous silica [24], further suggesting the presence of altered glass in these rocks. Iron mineralogy calculated from the Mössbauer spectrometer indicates that Fe was not present in volcanic glass in these rocks [25], suggesting the glass was pervasively altered such that the Fe was mobilized and removed from the glass or precipitated as secondary iron oxides.

The CheMin XRD on MSL detected ~30 wt.% X-ray amorphous material in the Rocknest soil [26]. The chemical composition of the amorphous component was calculated using mineral models from CheMin data and APXS bulk chemistry. These models predicted that the amorphous component is Fe- and S-enriched and Si-poor relative to a basalt composition [27,28]. Mineralogy derived from the Rocknest CheMin XRD data using a modified FULLPAT model includes basaltic glass as the main amorphous component; however, this result is inconsistent with the modeled chemical composition of the bulk amorphous component [26]. We suggest the composition is consistent with three different amorphous phases: 1) elevated Fe in the amorphous component, compositional similarities between the bulk Rocknest soil and soils in Meridiani and Gusev, and the identification of nanophase iron oxide (npOx) in soils at Meridiani and Gusev suggest a npOx phase [27,28]; 2) elevated S suggests an S-bearing phase; and 3) the presence of Si suggests an amorphous silicate phase (potentially altered glass, or a Fe-Si gel similar in composition to hisingerite [28,29]).

Conclusions and Further Questions: Both primary (volcanic/impact glasses) and secondary (opal/silica, allophane, hisingerite, npOx, S-bearing) amorphous phases appear to be major components of martian surface materials based on orbital and *in-situ* measurements. A key observation is that whereas regional/global scale amorphous components include altered glass and npOx, local scale amorphous phases include hydrated silica/opal. This suggests widespread alteration at low water-to-rock ratios, perhaps due to snow/ice melt with variable pH, and localized alteration at high water-to-rock ratios. Orbital and *in-situ* measurements of the regional/global amorphous component on Mars suggests that it is made up of at least three phases: npOx, amorphous silicate (likely altered glass), and an amorphous S-bearing phase.

Fundamental questions regarding the composition and the formation of the regional/global amorphous component(s) still remain: Do the phases form locally or have they been homogenized through aeolian activity and derived from the global dust? Is the parent glass volcanic, impact, or both? Are the phases separate or intimately mixed (e.g., as in palagonite)? When did the amorphous phases form? To address the question of source (local and/or global), we need to look for varia-

tions in the different phases within the amorphous component through continued modeling of the chemical composition of the amorphous phases in samples from Gale using CheMin and APXS data. If we find variations (e.g., a lack of or enrichment in amorphous silicate in some samples), this may imply a local source for some phases. Furthermore, the chemical composition of the weathering products may give insight into the formation mechanisms of the parent glass (e.g., impact glasses contain higher Al and lower Si [30], so we might expect allophane as a weathering product of impact glass). To address the question of whether these phases are separate or intimately mixed, we need to do laboratory studies of naturally altered samples made up of mixed phases (e.g., palagonite) and synthetic single phases to determine their short-range order structures and calculate their XRD patterns to use in models of CheMin data. Finally, to address the timing of the alteration, we need to study rocks on the martian surface of different ages that may contain glass (volcanic or impact) with MSL and future rovers to better understand how glass alters on the martian surface, if that alteration mechanism is universal, and if alteration spans across long periods of time or if there is a time past which unaltered glass remains.

References: [1] D. L. Evans and J. B. Adams (1979) *LPS X*. [2] R. B. Singer (1985) *Adv. Space Res.*, 5, 59-68. [3] D. L. Evans and J. B. Adams (1980) *LPS XI*. [4] R. V. Morris et al. (2000) *JGR*, 105, E1. [5] R. A. Binns (1967) *Nature*, 213, 1111-1112. [6] H. Y. McSween (1994) *Meteoritics*, 29, 757-779. [7] R. G. Burns (1993) *GCA*, 57, 4555-4574. [8] R. Hesse (1989) *Earth Sci. Rev.*, 26, 253-284. [9] O. A. Chadwick et al. (2003) *Chem. Geol.*, 202, 195-223. [10] C. C. Allen et al. (1981) *Icarus*, 45, 347-369. [11] R. B. Singer (1982) *JGR*, 87, B12. [12] J. L. Bandfield et al. (2000) *Science*, 287, 1626-1630. [13] M. B. Wyatt and H. Y. McSween (2002) *Nature*, 417, 263-266. [14] S. W. Ruff (2004) *Icarus*, 168, 131-143. [15] M. D. Kraft et al. (2003) *GRL*, 30, 24. [16] B. Horgan and J. F. Bell (2012) *Geology*, 40, 391-394. [17] E. B. Rampe et al. (2012) *Geology*, 40, 995-998. [18] R. E. Milliken et al. (2008) *Geology*, 36, 847-850. [19] J. L. Bandfield (2008), *GRL*, 35, 12. [20] B. H. Ehlmann et al. (2009) *JGR*, 114, E2. [21] S. W. Squyres et al. (2008) *Science*, 320, 1063-1067. [22] S. W. Ruff et al. (2011) *JGR*, 116, E7. [23] S. W. Ruff et al. (2006) *JGR*, 111, E12. [24] D. W. Ming et al. (2006) *JGR*, 111, E2. [25] R. V. Morris et al. (2008) *JGR*, 113, E12. [26] D. L. Bish et al. (2013) *Science*, 341, 6153. [27] D. F. Blake et al. (2013) *Science*, 341, 6153. [28] R. V. Morris et al. (2014) *LPS XLIV*. [29] E. Dehouck et al. (2014) *LPS XLIV*. [30] V. Bouska and J. F. Bell (1993) *JGR*, 98, E10.