ARE NOACHIAN/HESPERIAN ACIDIC WATERS KEY TO GENERATING MARS' REGIONAL-SCALE ALUMINUM PHYLLOSILICATES? THE IMPORTANCE OF JAROSITE CO-OCCURRENCES WITH AL-PHYLLOSILICATE UNITS. B. L. Ehlmann[1,2] and M. Dundar[3], [1]Division of Geological and Planetary Science, California Institute of Technology, Pasadena, CA, USA (ehlmann@caltech.edu). [2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA. [3]Dept. of Computer & Information Science, Indiana University-Purdue University, Indianapolis, IN, USA

Introduction: Compositionally stratified terrains with Al-phyllosilicates atop Fe/Mg-phyllosilicates have been found with orbital visible/shortwave infrared (VSWIR) imaging spectroscopy in several regions of Mars, at times with contiguous stratigraphy extending regionally over hundreds of thousands of kilometers [1-11]. Aluminum phyllosilicates can form from high water:rock ratio leaching of basaltic rocks, as products of alteration of siliceous precursors that can be less intensive than those required for a basaltic protolith, or acidic alteration of rocks of any type [3-13] (Fig. 1). The chemistry of the fluids and quantity and duration of water involved dictates whether these environments were habitable. Geomorphological and mineralogical evidence has, to date, been equivocal in establishing the origins of Mars' regional-scale Al phyllosilicate-bearing units. However, resolving the question of origin is important because the stratigraphies with Al phyllosilicates occur preferentially in late Noachian units but not earlier or later, at least at spatial scales visible from orbit. This suggests either wetter conditions and possibly a more clement climate enabling near-surface water for alteration that was temporally restricted to the late-Noachian/Hesperian boundary or a bias in unit preservation [13].

Here we re-examine the question of origin by consideration of mineral assemblages within Al phyllosilicate-bearing units (Fig. 1), using more advanced, automated techniques for endmember discrimination within high spatial resolution Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) VSWIR images [14-15] combined with traditional mapping of absorption band strengths. We show that jarosite—an indicator mineral for acidic, oxidizing conditions—is common in several Al phyllosilicate deposits. This suggests that acidic waters, rather than simply intensive leaching from high throughput of near-surface waters, were importantl to the development of these stratigraphies,

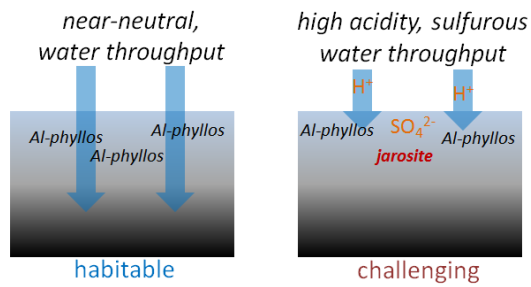
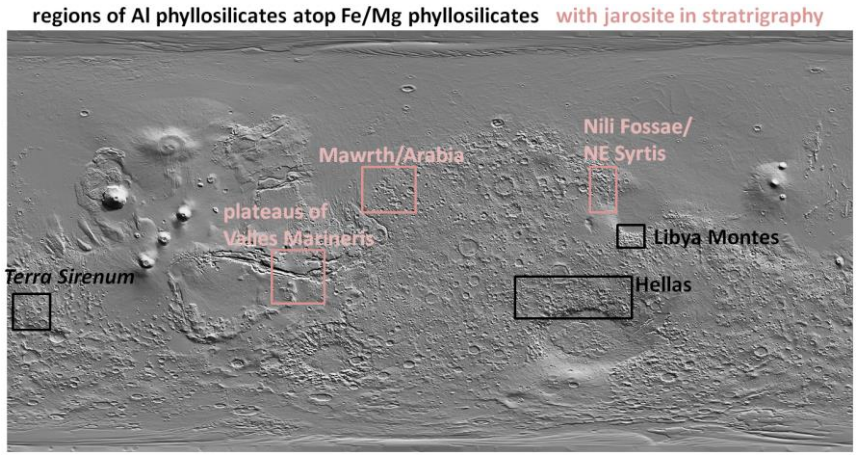


Figure 1. Two schematics for possible water chemistries and minerals formed during Al phyllosilicate formation. Whether or not waters were acidic is critical to understanding the habitability of the surface environment.

indicating regionally or globally significant regions of "acid Mars" during the late Noachian/early Hesperian.

Methods: Al phyllosilicates were first recognized in Mars Express/OMEGA data [1] due to prominent Al-OH absorptions at 1.40-1.41 µm and 2.20-2.21 µm [17-18], which subsequent CRISM data showed comprised a collection of multiple, discrete minerals with different absorption band shapes and positions, including montmorillonite [1], kaolinite [5,19], and beidellite [20], sometimes with intermixed additional phases, perhaps silica [21]. These phases all map with the standard CRISM BD2200 parameter [22]. The parameter formulation results also in mapping of other materials with absorptions near 2.2 µm, such as gypsum, jarosite, and alunite. This lumping of discrete, environ-

Figure 2. In several locations with the characteristic stratigraphy of Al phyllosilicates atop Fe/Mg phyllosilicates, jarosite has been found in associationwith the Al-phyllosilicate unit (Fig. 3; 11; 25). Terra Sirenum hosts jarosite in sediments within paleolakes but it has not yet been found in plateau phyllosilicates. Libya Montes and Hellas are still to be examined in our global survey.



mentally significant phases necessitates a new approach to exploration of spectral variability and recognition of mineral assemblages within the "Al phyllosilicate" units. In particular, driven by initial results [23] we have undertaken a systematic global search for the acid sulfate minerals alunite ($(K,Na)Al_3(SO_4)_2(OH)_6$) and jarosite ($(K,Na, H_3O^+)Fe_3(SO_4)_2(OH)_6$) within Al phyllosilicate-bearing units (Fig. 1). Alunite, jarosite, and intermediate phases in their solid solution have characteristic absorptions at 2.16 µm and 2.27 µm, respectively, that vary with cation substitution [24].

Areas with reported regional-scale occurrences of aluminum phyllosilicates were compiled from the literature [e.g. 10, 13]. CRISM L detector images were photometrically and atmospherically corrected using standard techniques [16]. Images were then processed to isolate endmembers using a non-parametric Bayesian clustering algorithm that can operate under weak assumptions regarding data characteristics and origin [14]. The algorithm divides each image data into several contiguous segments and analyzes all segments locally and jointly to identify spectral signatures representing endmembers, systematically using probabilistic sampling techniques. The underlying data model for each image segment is based upon the infinite mixture of infinitely many Gaussians, offering great flexibility in modeling skewed and multi-mode distributions [15].

Spectral signatures identified by this algorithm were cross-checked with existing VSWIR spectral libraries of minerals to identify phases and then spatially mapped using a custom parameter set.

Results: As part of our new global survey we began with the Al phyllosilicate regional units for which acid sulfates had not been reported and discovered 3 images with a dozen discrete outcrops showing evidence of jarosite co-occurrences with kaolin family minerals around Nili Fossae (e.g. Fig. 3). Jarosite has also been reported associated with plateau-style Al phyllosilicates at Mawrth Vallis [25] and in Valles Marineris [11], sometimes associated with silica instead [29]. Al phyllosilicates and jarosite are additionally found in paleolake sediments [26, 27] in Terra Sirenum, within Valles Marineris sediments [28].

Conclusions and Future Work: We will continue to systematically explore Al phyllosilicates above Fe/Mg phyllosilicates from the Martian rock record. Our initial data, coupled with the work of others [11, 25-29] suggests that these regional scale rock units may not merely reflect weathering sequences in a warm, wet early Mars climate, but rather the product of acidic (pH<4) waters interacting with the Martian surface. Future work will determine the implications for near-surface habitability during the Noachian and Hesperian as our survey continues and the stratigraphic relationships between the Al-phyllosilicate and jarosite-bearing patches are refined at each locale.

References: [1] Poulet et al., 2005, *Nature* [2] Loizeau et al., 2007, *JGR* [3] Bishop et al., 2008, *Science* [4] Wray et al., 2008, *GRL* [5] Ehlmann et al., 2009, *JGR* [6] Murchie et al., 2009, *JGR* [7] Loizeau et al., 2010, *Icarus* [8] Noe Dobrea et al., 2010, *JGR* [9] Carter et al., 2013, *JGR* [10] Loizeau & Carter, *Mars 8*, abs. #1203 [11] LeDeit et al., 2012, *JGR* [12] Horgan et al., *LPSC 44*, #3059 [13] Ehlmann et al., 2011, Nature [14] Dundar et al., 2014,BMC Bioinformatics [15] Yerebakan et al., 2014, NIPS [16] Murchie et al., 2009, *JGR* [17] Crowley & Vergo, 1988, *Clays & Clay Min.* [18] Clark et al., 1990, *JGR* [19] Mustard et al., 2008, *Nature* [20] Bishop et al., 2012 [21] McKeown et al., 2009, *JGR* [22] Pelkey et al., 2007, *JGR* [23] Dundar et al., 2013, IEEE WHISPERS [24] McCollom et al., 2014, *Am. Min* [25] Farrand et al., 2009 ; 2014, *Icarus* [26] Swayze et al., 2007, *Eos Trans. AGU 89(53)* [27] Wray et al., 2011, *JGR* [28] Thollot et al., 2012, *JGR* [29] Milliken et al., 2008, *Geology* [30] Clark et al., 2007, USGS Spectral Library (online)

Figure 3. (a) map of mixed Al phyllosilicates and jarosite atop Fe/Mg phyllosilicates (R: BD2270, G: D2300. B: BD2200) (b, c) HiRISE PSP_006989_2025 and (d) spectra from the CRISM image and the USGS spectral library [30]