

Chapter 3

A GLOBAL SURVEY OF ALUMINUM PHYLLOSILICATE FORMATION ACROSS MARS: ORIGIN FROM ALUMINOUS VOLCANICLASTIC ALTERATION AND BASALT LEACHING

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Abstract

Aluminum-phyllsilicates have been detected across Mars' Noachian (~3.7 Ga) terrains. They are typically found overlying Fe/Mg-phyllsilicates in a sequence proposed to have formed globally from pedogenic leaching of basalt. However, regional-specific studies suggest diversity between these Al-phyllsilicate regions. For example, some Al-phyllsilicates are detected alongside jarosite-alunite indicating strongly acidic alteration, and many lack expected associated Fe oxide. We conducted a survey of six Al-phyllsilicate-bearing regions across Mars, using CRISM hyperspectral imagery to map key alteration phases across these regions. We combine these maps with high-resolution imagery to examine their stratigraphic relationships. We find that these Al-phyllsilicate-bearing regions are consistent with two distinct formation processes. In Hellas Planitia, Eridania Basin, and parts of Mawrth Vallis, Al-phyllsilicate, often mixed with Fe oxide, conformably contacts and overlies Fe/Mg-phyllsilicate of the same texture. This is consistent with pedogenic leaching of basalt. Conversely, in Nili Fossae, Libya Montes, Terra Sirenum, Valles Marineris, and some locations in Mawrth Vallis, we find that Al-phyllsilicate, often mixed with jarosite and occasionally alunite, occurs in units of distinct texture to the Fe/Mg-phyllsilicate with unconformable contacts between. We conclude that in these regions, Al-phyllsilicate and jarosite-alunite most likely formed from alteration of a reworked airfall deposit of aluminous volcanic ash. These observations suggest that intensive near-surface weathering was restricted to a few locations across Mars, and elsewhere likely an order of magnitude less cumulative aqueous activity was required to produce the observed alteration. These results also indicate that Al-phyllsilicate evidences more extensive explosive and evolved volcanism than previously thought.

1 Introduction

Phyllsilicate (clay) minerals in Mars' Noachian terrains provide a mineralogic record of ancient water-rock interactions on the planet, recording ancient climate and rock and water chemistry (e.g. Poulet et al., 2005; Mustard et al., 2008). Fe/Mg-

phyllosilicates, e.g., smectite (Fe endmember nontronite to Mg endmember saponite), have been detected across Mars in widespread deposits on surfaces dated to the late Noachian–early Hesperian, which indicates widespread aqueous alteration. These minerals were detected with the hyperspectral infrared spectrometers OMEGA (Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité) on board the Mars Express orbiter (Poulet et al., 2005), and CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) on board the Mars Reconnaissance Orbiter (Mustard et al., 2008).

Al-phyllosilicates including kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and montmorillonite ($(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n(\text{H}_2\text{O})$) have also been detected in more localized deposits across Mars’ late Noachian–early Hesperian terrains. In particular, Al-phyllosilicate has been observed overlying Fe/Mg-phyllosilicate in six select regions (Carter et al., 2015): Nili Fossae (Ehlmann et al., 2009), Libya Montes (Bishop et al., 2013; Carter et al., 2015), Hellas Planitia (Carter et al., 2015), Terra Sirenum (Wray et al., 2011; Leask et al., 2024), Valles Marineris (Roach et al., 2010; Le Deit et al., 2012), and Mawrth Vallis (Loizeau et al., 2007; Wray et al., 2008; Noe Dobrea et al., 2008). These stratigraphic sequences of Al-phyllosilicate overlying Fe/Mg-phyllosilicate have often been interpreted to be pedogenic leaching sequences from a basaltic protolith, with Al-phyllosilicate representing a high degree of aqueous alteration (e.g., Ehlmann et al., 2009, Michalski et al., 2013; Carter et al. 2015; Klidas et al., 2025), and they have been found to be positively correlated with regions where chemical weathering would be expected to dominate over physical erosion (Moore et al., 2025).

Basalt is the most common rock type on Mars (McSween, 2009), and when it weathers on Mars or Earth, Fe/Mg-phyllosilicates are expected to form first from alteration of pyroxene and olivine, followed by the formation of Al-phyllosilicate from alteration of feldspar (Chevrier et al., 2007; Velde and Meunier, 2008). When basalt weathers under oxidizing and neutral-pH conditions, soluble cations such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} are leached from the system, and Fe^{3+} phyllosilicates such as nontronite are thermodynamically favored to form (Chevrier et al., 2007; Velde and Meunier, 2008; Catalano, 2013). If aqueous alteration continues, Al-phyllosilicates such as kaolinite and montmorillonite can then form in the next stage of the pedogenic leaching sequence (Velde and Meunier, 2008). Under oxidizing conditions, Fe oxides form alongside these

phyllosilicates (Nesbitt and Young, 1989; Gaudin et al., 2005; Greenberger et al., 2012). Fe^{2+} is more mobile than Fe^{3+} and can be leached during alteration under reducing conditions, inhibiting the formation of Fe oxides. Additionally, even Fe^{3+} can be mobilized in the process of acidic alteration and likewise inhibit Fe oxide precipitation (Blesa and Maroto, 1986). Under sufficiently acidic and sulfurous alteration, sulfates like jarosite and alunite are expected to form (Symonds et al., 1994). Alternatively, Al-phyllosilicate could form from a protolith that is originally more aluminous and distinct from the Fe/Mg-phyllosilicate (e.g., Wray et al., 2008; Bishop and Rampe, 2016; Leask et al., 2024).

Minerals in the jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) to alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) solid solution have been detected in conjunction with Al-phyllosilicates in several of these regions. Jarosite has been detected alongside Al-phyllosilicates in Nili Fossae (Ehlmann and Dundar, 2015; Baker and Ehlmann, in review), Valles Marineris (Roach et al., 2010; Weitz et al., 2011; Thollot et al., 2012), and Mawrth Vallis (Farrand et al., 2009; Farrand et al., 2014; Bishop et al., 2020), and alunite has been detected in Terra Sirenum (Swayze et al., 2008; Wray et al., 2011; Ehlmann et al., 2016; Leask et al., 2024), Valles Marineris (Viviano et al., 2013), and Mawrth Vallis (Miura et al., 2019; Poulet et al., 2020; Bishop et al., 2023). Jarosite and alunite form in acidic and oxidizing conditions. Jarosite typically forms at $\text{pH} < \sim 4.5$, and alunite typically forms at $\text{pH} < \sim 6.5$. In sufficiently acidic environments, the relative abundance of the two endmembers depends on the ratio of available Fe to Al (Symonds et al., 1994; Poulet et al., 2009; Ehlmann et al., 2016). In terrestrial environments, these minerals often form from the alteration of sulfide-containing rocks (Stoffregen, 1993; Bladh 1982; Alpers et al., 1992; Mavris et al., 2018), precipitation out of hypersaline acidic lakes (Long et al., 1992), or from fumarolic sulfurous gas – rock interactions (Stoiber and Rose, 1974; Zimbelman et al., 2005). The co-occurrence of these minerals with Al-phyllosilicate suggests that these minerals may have formed by weathering or hydrothermal alteration under acidic conditions.

Additionally, much of the Al-phyllosilicate on Mars lacks associated Fe oxide, which is unexpected for basaltic alteration in an oxidizing environment (Nesbitt and Young, 1989; Gaudin et al., 2005; Greenberger et al., 2012). Fe oxide has been reported in association with Al-phyllosilicate in parts of Mawrth Vallis (Wray et al., 2008), but it

has been searched for and not detected alongside Al-phyllsilicate in Valles Marineris (Le Deit et al., 2012) and Nili Fossae (Baker and Ehlmann, in review). In most Al-phyllsilicate bearing regions, however, the association of Al-phyllsilicate with Fe oxide has not yet been examined. This positive or negative detection of Fe oxide within the Al-phyllsilicate-bearing units is essential to help understand the pH and redox state of the alteration environment as well as the original availability of Fe in the system.

In this work, we reexamine Al-phyllsilicate and its associated alteration minerals across the six regions of Nili Fossae, Libya Montes, Hellas Planitia, Terra Sirenum, Valles Marineris, and Mawrth Vallis, applying the same methodology in all regions to enable robust, uniform comparisons between them. We implement an automated mineral identification pipeline that uses Gaussian fitting to detect and map Al-phyllsilicate, Fe/Mg-phyllsilicate, hydrated silica, jarosite, alunite, and Fe oxides in CRISM images across these regions. We examine these mineral maps alongside high-resolution images to determine the stratigraphic relationships and geologic contexts of these mineral deposits. We use the data to evaluate the formation of Al-phyllsilicate in each region and compare these geologic histories to understand the multiple processes and conditions of Al-phyllsilicate formation at a global scale across Mars. Finally, we discuss the implications of these proposed formation histories for Mars' climate and hydrology as well as its volcanism.

2 Previous Studies of Al-Phyllsilicate Regions

There have been numerous detailed local studies of the Al-phyllsilicate, and, where applicable, jarosite–alunite, for most of these regions of interest. These studies have revealed complexities that reflect local processes and chemistry. In some cases, these studies contradict the observations that would be expected if Al-phyllsilicate formed from basalt as part of a pedogenic leaching sequence.

In Nili Fossae, there is widespread Al-phyllsilicate stratigraphically overlying Fe/Mg-phyllsilicate. Previous studies interpreted this stratigraphy to represent basaltic weathering sequences (Ehlmann et al., 2009). However, that analysis was before the detection of some jarosite deposits in the region (Ehlmann and Dundar, 2015), and

without the most recent CRISM and HiRISE images. We therefore re-examined the Al-phylllosilicate in the context of its relationship to jarosite and with all available imagery. We found that the Al-phylllosilicate in this region is better explained by formation from an Al/Si-rich volcanoclastic sediment (e.g., ash) layer that was unconformably deposited on top of the Fe/Mg-phylllosilicate basaltic protolith. This is evidenced by the differences in texture between Al-phylllosilicate and Fe/Mg-phylllosilicate and several observed sharp contacts between them with no mixing at the CRISM resolution (18 m/pixel), and in some cases, there is spectrally bland material exposed between these phylllosilicates. Additionally, Al-phylllosilicate lacks the associated Fe oxide that would be expected if it formed from leaching of basalt under oxidizing conditions. Al-phylllosilicate is preferentially associated with topographic lows that form sedimentary basins, and it is often in m-scale layers within plateaus that also suggest its formation from sedimentary material. We detected sparse jarosite throughout the region, and it is associated with Al-phylllosilicate rather than Fe/Mg-phylllosilicate. This association of an Fe sulfate with only Al-phylllosilicate is unexpected if there was widespread acidic alteration in the region. Therefore, we argue that the requisite S to produce jarosite from Fe-bearing waters was likely locally-sourced from the Al-phylllosilicate ash protolith (Baker and Ehlmann, in review). No alunite has been reported in this region.

Analysis of Libya Montes is made difficult by the extensive dust cover, but studies have identified Al-phylllosilicate in several locations. Fe/Mg-phylllosilicate, thought to have formed from alteration of Noachian basalt, is widespread in this region (Bishop et al., 2013). Smaller deposits of Al-phylllosilicate have also been identified largely in eroded massif blocks or fluvial deposits, but they appear to be separate from the Fe/Mg-phylllosilicate-bearing units (Erkeling et al., 2012; Bishop et al., 2013). The Al-phylllosilicate has been identified as beidellite $((\text{Na}, \text{Ca}_{0.5})_{0.3} \text{Al}_2((\text{Si}, \text{Al})_4 \text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O})$, which often forms at higher temperatures than other Al-phylllosilicates like montmorillonite or kaolinite. Therefore, the beidellite may represent local hydrothermal conditions or burial diagenesis (Bishop et al., 2013). No jarosite or alunite has been reported in this region, and Fe oxide distribution has not been examined

Al-phylllosilicate has been detected in the plains north of Hellas Planitia (Carter et al., 2015), but it has not been extensively studied. Fe/Mg-phylllosilicate occurs across the

region in Noachian sedimentary plains deposited by fluvial and aeolian processes (Ansan et al., 2011; Carter et al., 2011; Salese et al., 2016). Several deposits of Al-phyllsilicate, both montmorillonite and kaolinite, have been found in this region alongside Fe/Mg-phyllsilicate, where they are thought to have formed as a part of a weathering sequence (Carter et al., 2011; Carter et al., 2015). No jarosite or alunite has been reported in this region, and the Fe oxide distribution has not been examined.

Previous studies have indicated that Al-phyllsilicates in Terra Sirenum formed through two distinct processes. Eridania Basin is a possible ancient sea in the region that contains phyllsilicates that may have formed through marine hydrothermal alteration (Irwin et al., 2004; Michalski et al., 2017; Hughes et al., 2024). Here, thin, unlayered Al-phyllsilicates including kaolinite and montmorillonite are observed overlying Fe/Mg-phyllsilicates in what are purported weathering sequences from altered Hesperian volcanic basin-filling material (Noe Dobrea et al., 2008; Adeli et al., 2015; Pajola et al., 2016; Leask et al., 2024). Jarosite is associated with Fe/Mg-phyllsilicate and some Al-phyllsilicate in this region, and alunite is associated with some Al-phyllsilicate. These minerals are found primarily in veins, indicating possible acidic groundwater interactions and/or alteration of sulfides (Pajola et al., 2016; Michalski et al., 2017; Leask et al., 2024; Hughes et al., 2024). Hematite has been reported in this region from the Mars Global Surveyor Thermal Emission Spectrometer (Hughes et al., 2024), though its relationship to the Al-phyllsilicates has not been examined.

Outside of Eridania Basin, thick (60–150 m) Al-phyllsilicates are found across the region, largely in impact craters (Wray et al., 2011; Ehlmann et al., 2016; Leask et al., 2024). Fe/Mg-phyllsilicates are found in crater ejecta, indicating its presence at depth but with limited exposures at the surface (Leask et al., 2024). The Al-phyllsilicate, largely kaolinite with some montmorillonite, demonstrates increasing thickness of the unit towards the volcano Arsia Mons and often has m-scale layers. Because of this, it has been interpreted to have formed from alteration of a volcanic ash deposit emplaced unconformably over the Fe/Mg-phyllsilicate protolith (Leask et al., 2024), similar to our conclusion for Al-phyllsilicate formation in Nili Fossae (Baker and Ehlmann, in review). Alunite is found within some of the Al-phyllsilicate across the region (Swayze et al., 2008; Ehlmann et al., 2016; Leask et al., 2024). It has been interpreted to have

formed from the upwelling of acidic groundwater, possibly acidified through interaction with S-enriched magma (Ehlmann et al., 2016; Leask et al., 2024). Fe oxide has not been reported in this region.

In Valles Marineris, Al-phyllsilicate is found in three different contexts purportedly explained with three formation mechanisms. On the plateaus and plains surrounding eastern Valles Marineris, Fe/Mg-phyllsilicate is detected in laterally extensive Noachian units. Patchy Al-phyllsilicate (montmorillonite, beidellite, and kaolinite) is reported overlying the Fe/Mg-phyllsilicate (Le Deit et al., 2012). Due to this stratigraphy, these units have been interpreted to represent extensive top-down pedogenic leaching, most likely of a basaltic protolith. No jarosite or alunite has been detected in these so-called “plateau phyllsilicates,” and Fe oxide was searched for and not reported (Le Deit et al., 2012). In Noctis Labyrinthus in western Valles Marineris, a possibly distinct, dominantly kaolinite Al-phyllsilicate unit is exposed *underlying* the Fe/Mg-phyllsilicate, an unusual stratigraphy on Mars. Here, jarosite is locally associated with some Al-phyllsilicate. These minerals are proposed to have formed from alteration by groundwater with a changing chemistry including S-bearing acidic fluids from magmatic sources (Roach et al., 2010; Weitz et al., 2011; Thollot et al., 2012). In the main chasms of Valles Marineris, there are scattered exposures of Fe/Mg-phyllsilicate (Roach et al., 2010). Al-phyllsilicate has been tentatively detected throughout the region in so-called “doublet material.” This hydrated material has a spectral signature with a doublet absorption at 2205–2218 and 2265–2278 nm. Multiple hypotheses have been proposed for the composition of this material including a mixture of Al-phyllsilicate and/or hydrated silica with jarosite or Fe/Mg-phyllsilicate, gypsum or an alternative sulfate, or acid-altered Al/Fe-phyllsilicate (e.g. Tosca, 2008; Roach et al., 2010). Alunite has been detected in two locations in Valles Marineris alongside hydrated silica and possible Al-phyllsilicate (Viviano et al., 2013). Abundant Fe oxide has been detected within the Valles Marineris chasms in association with sulfate (Le Deit et al., 2008; Roach et al., 2010), though its association with Al-phyllsilicate or the doublet material has not been examined.

The thickest Al-phyllsilicate deposits on Mars are found in Mawrth Vallis, though there is a lack of consensus on their formation processes. The Al-phyllsilicate

unit in this region is composed of two units, an upper kaolinite and lower montmorillonite unit. Both Al-phyllsilicates are likely mixed with a hydrated silica component (Bishop et al., 2008). The Al-phyllsilicate-bearing unit appears to be draped over the underlying Fe/Mg-phyllsilicates in a layer 10s of m thick (Wray et al., 2008; Loizeau et al., 2012; Klidas et al., 2025). Some studies conclude that the Al-phyllsilicate likely formed alongside the Fe/Mg-phyllsilicates as part of a pedogenic leaching sequence from a basaltic protolith (Loizeau et al., 2010; Michalski et al., 2013). Other studies conclude that there is an unconformity between Al-phyllsilicate and the underlying Fe/Mg-phyllsilicate, indicating possible formation from distinct protoliths (Wray et al., 2008; Bishop and Rampe, 2016). The Al-phyllsilicate is unlayered, and the draping in this case may be consistent with an airfall deposit such as of fine-grained pyroclastic material (Wray et al., 2008; Michalski et al., 2013; Klidas et al., 2025). The hydrated silica minerals allophane and imogolite have been detected overlying the Al-phyllsilicate, which on Earth often form from volcanic ash weathering (Bishop and Rampe, 2016). Jarosite has been detected overlying the Al-phyllsilicate in a few locations (Farrand et al., 2009; Farrand et al., 2014). “Doublet material” similar to that observed in Valles Marineris (Roach et al., 2010) has also been detected in Mawrth Vallis and has been attributed to mixed Al-phyllsilicate and jarosite (Bishop et al., 2020). This jarosite has been proposed to have formed by acidic brines released from melting ice (Michalski et al., 2013; Bishop and Rampe, 2016), as evaporites in small acidic ponds with dissolved S from volcanic gasses (Michalski et al., 2013; Bishop et al., 2020), or through alteration of a pyrite-bearing layer (Farrand et al., 2009). Small amounts of alunite have also been detected mixed with Al-phyllsilicate, sometimes in association with jarosite as well (Miura et al., 2019; Poulet et al., 2020; Bishop et al., 2023). Fe oxides including possible hematite and goethite have been reported to be mixed with some of the Al-phyllsilicate throughout this region (Wray et al., 2008) and to be mixed with jarosite (Farrand et al., 2009).

These reviews of the primary Al-phyllsilicate-bearing regions demonstrate that there is substantial complexity and diversity in their formation processes on a regional scale. Studies that address these Al-phyllsilicate-bearing regions on a global scale often treat all the Al-phyllsilicate as indicative of extensive weathering in a pedogenic

leaching sequences despite the variation in the mineralogy and stratigraphic configuration of Al-phylosilicate and accompanying phases across these regions (e.g. Carter et al., 2015; Moore et al., 2025; Klidas et al., 2025).

3 Methods

3.1 Data processing

We chose to examine map projected targeted reduced data record (MTRDR) CRISM images, which were atmospherically corrected and denoised as described in Murchie et al. (2007), Murchie et al. (2009), and Seelos et al. (2024). We examined all MTRDR images in six regions: five identified by Carter et al. (2015) as demonstrating widespread possible phyllosilicate weathering sequences (Nili Fossae, northern Hellas Planitia, Terra Sirenum, Valles Marineris, and Mawrth Vallis) and a sixth region, Libya Montes, which is not discussed in detail by Carter et al. (2015) but was noted by them as demonstrating this possible sequence in several locations. This totaled 1,976 MTRDR images.

To reduce column-specific noise in the spectral data, we calculated the ratio of every spectrum to the representative bland spectra in its image column. To identify these bland spectra, we used the method described in Baker and Ehlmann (in review), which was originally based on a method developed by Pan et al. (2017). In this method, the bland spectra in each column prior to map-projection were defined as those that had values below the mean + 1.5 * the standard deviation value in a column for these spectral parameters produced by Viviano et al. (2014): BD530_2, BD860_2, BD1400, OLINDEX3, LCPINDEX2, HCPINDEX2, BD1750_2, BD1900_2, BD2190, BD2250, BD2265, BD2290, and BD2355. For this study, we added an additional criterion that the value of BD2290 for a spectrum must be < 0.003 for that spectrum to be included in this bland pool. Without this additional criterion, Fe/Mg-phylosilicate-bearing spectra were occasionally included in the bland pool if a column had a sufficiently high areal coverage of Fe/Mg-phylosilicate (Baker and Ehlmann, in review), and this step worked to reduce this erroneous inclusion. Of these bland spectra, we then took the mean of those that had the 9

smallest integrated areas in the wavelength range 1869–2417 nm to be the denominator spectra for column ratioing. We then applied a Savitzky-Golay filter with a bin width of five channels and a polynomial order of two to each ratioed spectrum for additional denoising.

3.2 Mineral identification

We used these processed CRISM images to identify and map key alteration minerals of interest: Al-phylosilicate, Fe/Mg-phylosilicate, jarosite, alunite, hydrated silica, and Fe oxide (Table 1). We found that the conventional method of mapping the band depth of absorption features (e.g. Viviano et al., 2014), was not able to consistently identify these phases in mixtures, particularly jarosite. Therefore, we used the methods described by Baker and Ehlmann (in review) to identify these key alteration phases. We fit Gaussian curves to continuum-removed sections of the spectra to identify each mineral following the specifications listed in Table 2. We fit a single Gaussian to identify all minerals but jarosite. Because we found that jarosite frequently occurs in mixtures with Al-phylosilicate, we fit two Gaussian curves to the mixed doublet feature at ~2200 nm, with one fixed on the jarosite absorption position of 2264 nm and the other fixed to the Al-phylosilicate absorption position of 2205 nm. A pixel was considered to contain the mineral of interest if the depth of the fit Gaussian exceeded 3x the standard deviation of that column's bland spectrum in that wavelength range.

This process is very similar to the methods described in Baker and Ehlmann (in review), which were developed for application to Nili Fossae. We added several criteria to limit false negatives in other regions with lower Al-phylosilicate abundances and higher dust coverage. We automatically excluded pixels that did not meet numeric thresholds for the values of band depth parameters calculated for their ratioed spectra. We developed these parameters in the style of Viviano et al. (2014). These parameters include:

$$\begin{aligned}
& \text{BD2205(ratioed)} \\
& = 1 - \left(\frac{\frac{R_{2198.8} + R_{2205} + R_{2212.0}}{3}}{0.465 * \frac{R_{2145.9} + R_{2152.5} + R_{2159.1}}{3} + 0.535 * \frac{R_{2245.0} + R_{2251.6} + R_{2258.3}}{3}} \right) \\
& \text{BD2212 (ratioed)} = 1 - \left(\frac{R_{2212}}{0.593 * R_{2152.5} + 0.407 * R_{2298.0}} \right) \\
& \text{BD2311 (ratioed)} = 1 - \left(\frac{\frac{R_{2317.8} + R_{2324.4} + R_{2331.0}}{3}}{0.429 * R_{2238.4} + 0.571 * R_{2357.5}} \right)
\end{aligned}$$

In these equations, R_x represents the reflectance of the spectrum at a wavelength of x nm.

To separate identification of minerals with similar absorption positions such as Al-phyllsilicates including kaolinite and montmorillonite, alunite, and hydrated silica, we compared the center wavelength and width of the fit ~2200 nm Gaussian curve to those of Gaussian curves fit in the same way to laboratory endmembers, several key simulated linear mixtures of these laboratory phases as described by Baker and Ehlmann (in review). These endmembers include: kaolinite, montmorillonite, beidellite, opal-A and opal-C taken at atmospheric pressure and low (Mars-equivalent) pressure (Sun, 2017), illite, jarosite, and alunite. We plotted mixtures of kaolinite + jarosite and kaolinite + opal.

For each image where our generated mineral maps identified the presence of a mineral absorbing ~2200 nm, we drew regions of interest (ROIs) around a representative number of deposits of the mineral(s) in that image, capturing the spectral diversity. We extracted the mean spectra of each ROI, fit Gaussian curves to the mean spectra as we did for the individual pixel spectra and plotted these in center versus width parameter space. We plotted these parameters for all Al-phyllsilicate mean ROI spectra for each region.

To identify alunite, which is often mixed with Al-phyllsilicate and so can be difficult to isolate, we combined the above methods with examination of the wavelength of the minimum of the absorption feature and other diagnostic absorptions. Alunite has diagnostic absorptions at 1750 nm as well as 2165 nm. For each image that was found to contain a phase absorbing near 2200 nm, we examined by hand the respective map of the BD1750_2 parameter made by Viviano et al. (2014) to identify pixels with absorptions at

this position. We also generated maps in which we plotted the wavelength position of the minimum of the ~2200 nm absorption for all pixels identified as containing an absorption near this location. From these maps, we were able to identify pixels with absorption minima short what would be expected for Al-phyllsilicate alone. Spectra that contained these shorter ~2200 nm absorptions and an absorption at 1750 nm were identified as containing alunite.

Table 1

Relevant Minerals and Their Absorptions

Mineral group	Mineral name	Formula	Diagnostic absorption(s) (nm) used here	Cause of absorption
Al-phyllsilicate	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	2165 and 2205 doublet	Al-OH vibrational
	Montmorillonite	$(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2215	Al-OH vibrational
Fe/Mg-phyllsilicate	Nontronite	$\text{Na}_{0.3}\text{Fe}_2((\text{Si,Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2285	Fe-OH vibrational
	Saponite	$\text{Ca}_{0.25}(\text{Mg,Fe})_3((\text{Si,Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2315	Mg-OH vibrational
Sulfate group	Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	2265	Fe-OH vibrational
	Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$	2165	Al-OH vibrational
Hydrated silica	Opal	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	2210–2245 (broad)	Si-OH vibrational
Fe oxide/hydroxide	Hematite	Fe_2O_3	540	Fe electronic charge transfer
	Goethite	$\text{FeO}(\text{OH})$	490	Fe electronic charge transfer
	Ferrihydrite	$\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$	525	Fe electronic charge transfer
	Lepidocrocite	$\text{FeO}(\text{OH})$	490	Fe electronic charge transfer

Minerals targeted for identification by the Gaussian fitting algorithm and the wavelengths and causes of the diagnostic absorptions used by the algorithm for each mineral. Note that iron-bearing phases also have diagnostic absorptions between 800-1000 nm but these were not used for initial identification to avoid confusion with pyroxene, which also has absorptions in this wavelength range.

3.3 Examining stratigraphic relationships and geologic context

We used ArcGIS Pro for examining the stratigraphic relationships between geologic units identified in our mineral maps. We georeferenced these maps by hand to Mars Context Camera (CTX) 6 m/pixel images (Malin et al., 2007) and, where available, High Resolution Imaging Science Experiment (HiRISE) camera 0.25 m/pixel images (McEwen et al., 2007). We also used the 463 m/pixel Mars Orbital Laser Altimeter (MOLA) map to understand the topographic context (USGS). With these data, we observe and describe the stratigraphic contexts and contacts between Al-phyllsilicate, Fe/Mg-phyllsilicate, jarosite–alunite, and Fe oxide in the six regions across Mars.

Table 2

Mineral Identification Process and Criteria

Target mineral(s)	Number of Gaussian curves fit	Free variables	Pre-set variables	Wavelength range fit	Limits on center position	Other criteria
Al-phyllsilicate, hydrated silica, alunite	1	Depth, center wavelength, width	N/A	2112.87 nm – 2331.02 nm	2159.83 nm – 2279.98nm	BD2190 or BD2250 > 0.006 or BD2205(ratioed)>0.0035 or BD2212(ratioed)>0.0028 and LCPINDEX2 < 0.027 Once fit, exclude pixels with centers > 2250.02 nm
Fe/Mg-phyllsilicate	1	Depth, center wavelength, width	N/A	2245.04 nm – 2390.58 nm	2,304.15 nm – 2,400.38 nm	BD2290 > 0.004 or BD2311(ratioed) > 0.002
Jarosite	2	Depth, width	Center wavelengths	2112.87 nm – 2331.02 nm	Fixed at 2265.01 nm and 2205.07 nm	BD2265>0.003 and R2284.72>R2264.88

Fe oxide	1	Depth, center wavelength, width	N/A	442 nm – 631 nm	400 nm – 600 nm	BD530 > 0.16, fit Gaussian depth > BD625
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Details of the Gaussian fitting algorithm applied to identify each group of minerals, limits applied to free variables, and other criteria a spectrum had to meet to be considered to contain the relevant target mineral.

4 Results

4.1 Global distribution of Al-phyllsilicate and accompanying phases

We find widespread Al-phyllsilicate in the six regions examined here. In most cases, it appears to stratigraphically overlie Fe/Mg-phyllsilicate, consistent with prior observations (e.g. Poulet et al., 2005; Ehlmann et al., 2009; Le Deit et al., 2012; Carter et al., 2015; Klidas et al., 2025). However, in the chasms of Valles Marineris, Fe/Mg-phyllsilicate is not detected near the exposed Al-phyllsilicate. In Terra Sirenum, only sparse, scattered Fe/Mg-phyllsilicate is exposed, but it likely exists at depth beneath the Al-phyllsilicate.

We confirm prior detections of jarosite with Al-phyllsilicate in Nili Fossae (Ehlmann and Dundar, 2015), Terra Sirenum (Ehlmann et al., 2016; Hughes et al., 2024; Leask et al., 2024), Valles Marineris (Roach et al., 2010), and Mawrth Vallis (Farrand et al., 2009; Farrand et al., 2014; Bishop et al., 2020). We identify several new locations with detections of this mixture in each of these regions as well. We also corroborate prior detections and identify several new detections of jarosite associated with Fe/Mg-phyllsilicate in Terra Sirenum. Of the regions examined, Terra Sirenum is the only one in which we observe jarosite in association with Fe/Mg-phyllsilicate. We confirm and expand detections of alunite mixed with Al-phyllsilicate and/or hydrated silica in Terra Sirenum, Valles Marineris, and Mawrth Vallis, and searched for but did not find alunite in the other 3 regions.

The distribution of Fe oxide in association with Al-phyllsilicate is uneven across the globe. In Nili Fossae, Libya Montes, and eastern Terra Sirenum, we do not detect Fe oxide mixed with Al-phyllsilicate. We frequently see a mixture of Fe oxide with at least

some Al-phylosilicate exposures in Hellas Planitia, Eridania Basin, and Mawrth Vallis. In Valles Marineris, much of the Al-phylosilicate that is exposed at depth in the chasms is associated with Fe oxide. In this region, the Fe oxide is also strongly correlated with jarosite.

Hydrated silica distribution is also location dependent. In Nili Fossae, hydrated silica primarily occurs separately from the Al-phylosilicate. It is found to the west of the fossae, whereas the Al-phylosilicate is more concentrated around the fossae themselves. In Hellas Planitia, Terra Sirenum, and Mawrth Vallis, there is a small amount of hydrated silica, though less abundant than Al-phylosilicate. In these regions, it is detected both on its own and nearby Al-phylosilicate. In Valles Marineris, there is abundant hydrated silica exposed at depth in the chasms along with Al-phylosilicate, jarosite, and Fe oxide. We do not detect hydrated silica in Libya Montes.

4.2 Comparative spectral analysis of Al-phylosilicate and accompanying phases

4.2.1 Al-phylosilicate mineralogy

The specific mineralogy of Al-phylosilicate varies both between and within regions. We compare the mineralogy of Al-phylosilicate across Mars to laboratory measurements of the spectra of endmember minerals from ROIs from multiple locations in each region, focusing on the absorption center position and width. There is substantial overlap in these regions in this parameter space, though some illuminating distinctions emerge (Figure 1). For each region, we manually identify several endmembers that capture the spectral diversity of the Al-phylosilicate and its accompanying phases (Figure 2).

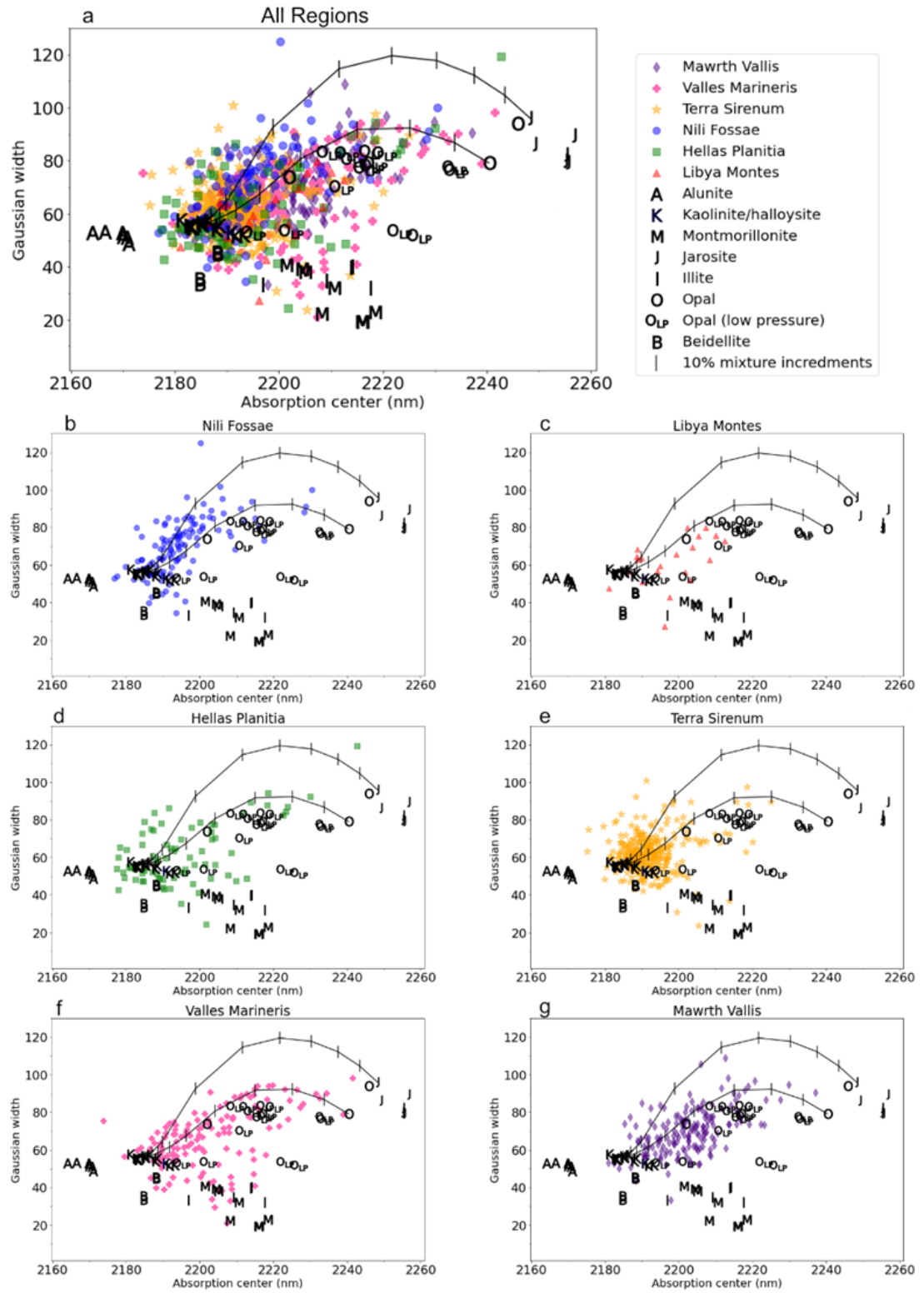


Figure 1: Scatterplots of the fit Gaussian width versus the fit Gaussian center position. Each point represents the fit to the mean spectrum of an ROI. Gaussian fits to laboratory spectra and two modeled linear mixtures are plotted for comparison. Laboratory spectra

were taken from USGS and RELAB, and low pressure opal measurements were taken from Sun (2017). a) All Al-phylosilicate ROIs we identified from every region. b-g) Scatterplots for each region shown in a plotted individually.

In Nili Fossae (Figure 1b, Figure 2b), the Al-phylosilicate is dominantly kaolinite, as indicated by the doublet at 2265 and 2200 nm. This kaolinite is clustered around laboratory endmember kaolinite in our scatter plot parameter space, though some of it plots with somewhat wider widths and longer wavelength Gaussian centers than laboratory kaolinite. We find that these points correspond to spectra that maintained the kaolinite doublet but may be wider due to mixing with an additional hydrated silica phase. In addition to kaolinite, we detect hydrated silica that is a close match for opal, jarosite, mixed jarosite + kaolinite, and a few deposits that appear most similar to beidellite. We also detect an ambiguous aluminosilicate with a wide, symmetric absorption centered at 2205 nm that we cannot match to a single endmember phase. These deposits plot near opal or kaolinite + opal in our scatterplot, though spectrally they do not appear to be a close match for those phases. Unique among the regions we examined here, Nili Fossae lacks a conclusive detection of montmorillonite.

Previous analysis of Libya Montes has reported Al-phylosilicate primarily in the form of beidellite (Bishop et al., 2013). In our analysis, we detect a deposit of possible beidellite as identified by its narrow symmetric absorption short of 2200 nm. However, we conclude that the Al-phylosilicate in this region is largely a better match for kaolinite or montmorillonite (Figure 1c, Figure 2c). We identify several deposits of an ambiguous wide, symmetric aluminosilicate that appears similar to what we observe in Nili Fossae, and these points also plot near opal on our scatterplots.

In Hellas Planitia (Figure 1d, Figure 2d), both kaolinite and montmorillonite appear to be common compositions for the Al-phylosilicate, though montmorillonite is more prevalent. We also detect a small number of possible beidellite deposits, as well as an aluminosilicate that is wide and symmetric but absorbs at ~2180 nm, short of the other aluminosilicates detected. The hydrated silica in this region is narrower than the opal detected in Nili Fossae.

Similar to Nili Fossae, we find that the Al-phylosilicate in Terra Sirenum (Figure 1e, Figure 2e) is dominantly kaolinite, though it also contains a small number of

montmorillonite detections. We also detect a wide aluminosilicate similar to that in Nili Fossae and Libya Montes, and we find hydrated silica. Like Nili Fossae, we identify jarosite as well as jarosite mixed with Al-phyllsilicate (likely kaolinite). We also detect alunite mixed with Al-phyllsilicate, as indicated by its broad absorption at ~2165 nm combined with an absorption at ~1750 nm not shown here.

Valles Marineris (Figure 1f, Figure 2f) contains both abundant kaolinite and abundant montmorillonite. Additionally, much of its Al-phyllsilicate occurs in mixtures with jarosite. These mixed jarosite points tend to plot along the trendline of our modeled linear kaolinite-opal mixture. They are slightly narrower than our modeled kaolinite-jarosite mixture, possibly due to the simplifications of a rudimentary linear mixture model. In addition to jarosite, we identify sparse alunite mixed with Al-phyllsilicate. We also identify hydrated silica and the wide, symmetric aluminosilicate phase.

In Mawrth Vallis (Figure 1g, Figure 2g), we find both kaolinite and montmorillonite, though the Al-phyllsilicate in this region is predominantly montmorillonite. Much of the montmorillonite is wider than the laboratory endmembers and plots closer to opal on our scatterplot, though it maintains montmorillonite's absorption position and distinctive symmetry. This may indicate that it is mixed with another silica phase. We identify mixed jarosite and alunite as well as apparently endmember jarosite. We observe alunite mixed with Al-phyllsilicate, similar to Terra Sirenum and Valles Marineris. We observe two ambiguous aluminosilicates in this region: we see one that absorbs at 2205 nm similar to that detected in most of the regions, and we see one that absorbs at shorter wavelengths of 2180 nm similar to Hellas Planitia.

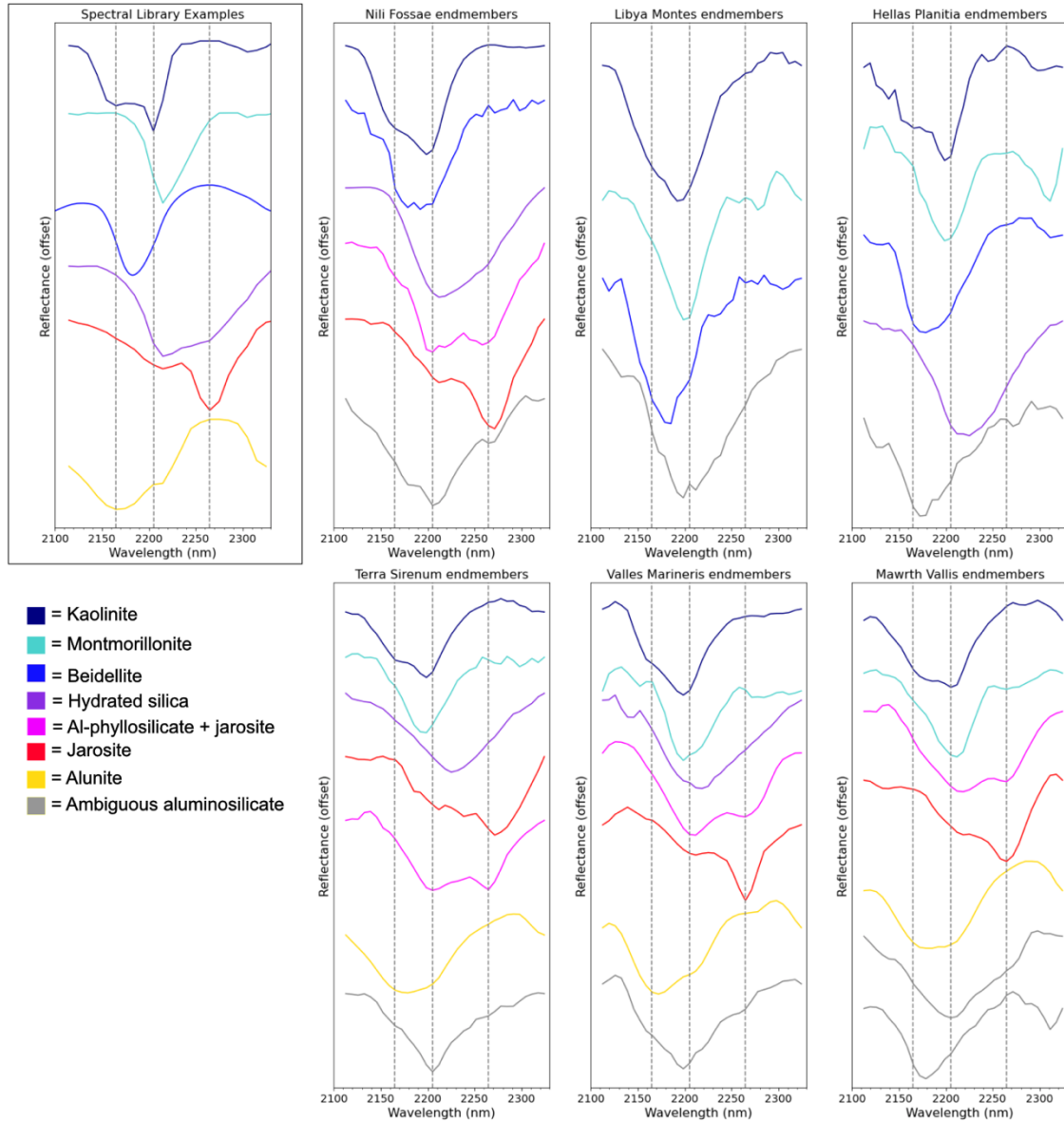


Figure 2: a) Endmember spectra of Al-phyllsilicate and associated minerals from laboratory spectral libraries and, b-g) manually selected from each region. All spectra were continuum-removed from 2100–2330 nm and normalized between 0–1 before being offset. Each CRISM endmember represents the mean spectrum of an ROI is colored based on our identification of it, with gray “ambiguous aluminosilicate” spectra lacking a clear match to any one laboratory endmember. Vertical dashed lines mark 2165 nm, 2205 nm, and 2265 nm.

4.2.2 Al-phyllsilicate + jarosite mixtures

In Terra Sirenum (Hughes et al., 2024), Valles Marineris (Roach et al., 2010), and Mawrth Vallis (Bishop et al., 2020), a so-called “doublet material” has been identified that has absorptions at 2205–2212 nm and 2265–2271 nm. This feature has been variously attributed to several different possible phases including a mixture of Al-phyllsilicate and jarosite, hydrated silica and jarosite, acid altered clay, and a mix of Al-phyllsilicate with Fe-phyllsilicate. Notably, in Nili Fossae, we see material with a similar doublet feature but where units also have areas with distinct kaolinite signatures and distinct jarosite signatures, leading us to conclude that this doublet feature represents a mixture of Al-phyllsilicate and jarosite in that region (Baker and Ehlmann, in review). We compare normalized, continuum-removed spectra of the purported Al-phyllsilicate + jarosite phase to the doublet phase from Terra Sirenum, Valles Marineris, and Mawrth Vallis. While the depths of the two absorptions can vary due to the abundances of the two minerals, by comparing the normalized continuum-removed spectra of this feature, we see these doublet phases across regions have very similar absorption positions, absorption feature widths, and overall structure (Figure 3). We therefore conclude that the doublet phase in these regions is also most likely a mixture of Al-phyllsilicate and jarosite. We contend that the 2265 nm feature is at too short of a wavelength to be explained by nontronite (Fe-smectite), which laboratory data show absorbing at 2290 at the shortest (Kokaly et al., 2017). While the doublet is similar to laboratory measurements of acid altered clays (Roach et al., 2010; Tosca, 2008), it is more similar to the spectra we most confidently attribute to mixed Al-phyllsilicate + jarosite in Nili Fossae.

In Valles Marineris, there is variation between spectra that are considered to have this doublet feature. While most of it has absorptions at ~2200 nm and ~2265 nm that we attribute to a mixture of Al-phyllsilicate and jarosite, we also observe a doublet with absorptions at 2218 nm and 2265 nm and a doublet with absorptions at 2205–2218 nm and 2284 nm. We interpret the doublet at 2218 and 2265 nm as a mixture of hydrated silica and jarosite, as it co-occurs with hydrated silica throughout the region. The cause of the 2284 nm absorption is unclear, but may be due to nontronite.

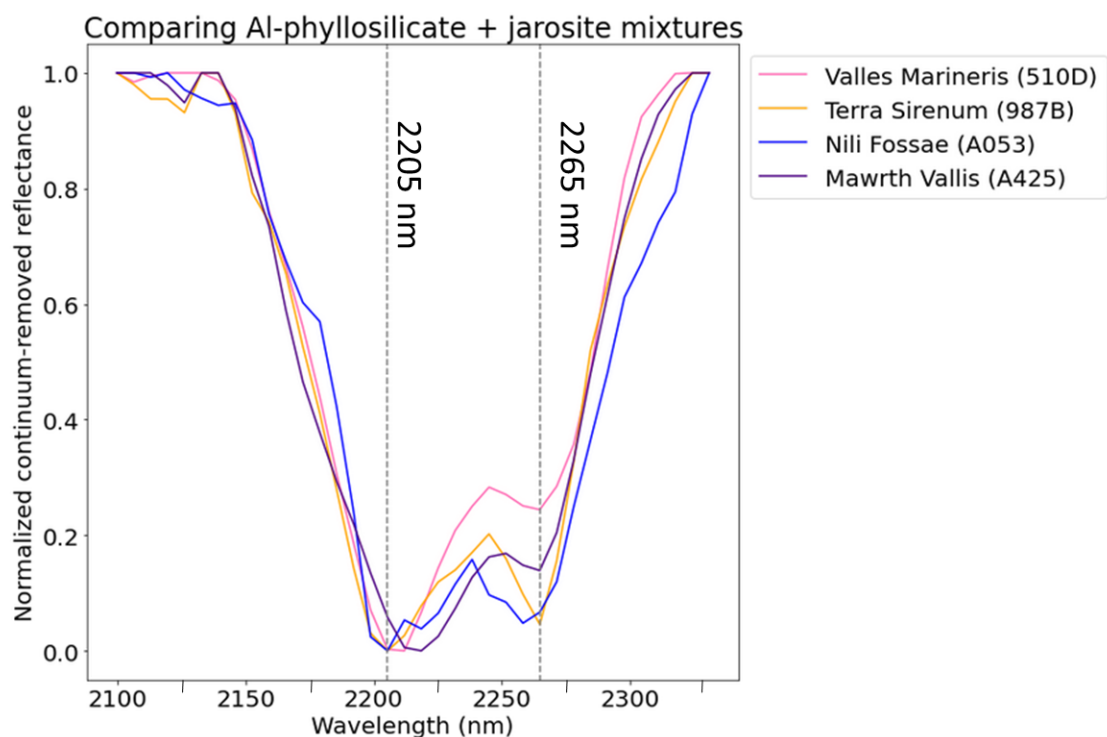


Figure 3: Example spectra of what we conclude is most likely mixed Al-phyllsilicate and jarosite in Valles Marineris, Terra Sirenum, Nili Fossae, and Mawrth Vallis. Each spectrum is the mean spectrum of an ROI taken from the listed image. Each spectrum was continuum-removed from 2100–2330 nm and normalized from 0-1 to allow comparison of the spectra irrespective of the absorption depths.

4.2.3. Fe oxide

We identify Fe oxide as a group of phases with one or two broad absorptions in the short range visible–near-infrared. These phases at least have a broad absorption centered around 500 nm that we attribute to Fe charge transfer, and most also have a second absorption from 890–920 nm that we attribute to an electronic Fe absorption. We plot an example of this phase where is observed mixed with Al-phyllsilicate in each region (Figure 4a) and compare it to laboratory Fe oxides and pyroxenes (Figure 4b) (Kokaly et al., 2017). There is variation in this phase with region, and most are not a clear match for a single Fe oxide phase. The Mawrth Vallis example spectrum is similar to crystalline red hematite, as it has absorptions centered at around 530 nm and 860 nm, but other examples lack similar laboratory spectra. We conclude that these phases are most likely a

mixture of multiple Fe-bearing phases, and we refer to it generally as Fe oxide. We excluded false positive detections of Fe oxide that appear to be due to a spectral artifact created by direct illumination of topographic faces.

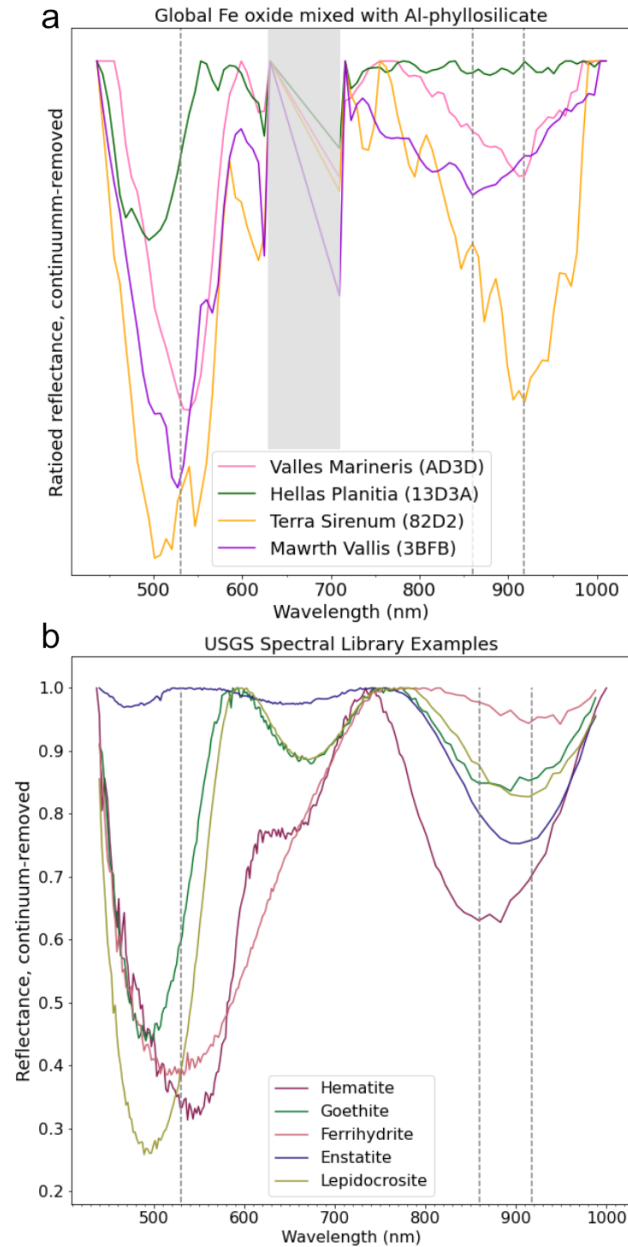


Figure 4: Representative examples of spectra of the minerals absorbing around 500 nm and/or 900 nm that are observed mixed with Al-phyllsilicate across Mars compared to laboratory samples. a) Short wavelength range continuum-removed mean spectra of all mixed Fe oxide and Al-phyllsilicate in the given image. The obscured area between 631

nm – 710 nm represents a CRISM filter break (Murchie et al., 2007). b) Continuum-removed spectra of Fe oxides and pyroxene taken in the laboratory from the USGS spectral library (Kokaly et al., 2017) for reference.

4.3 Stratigraphic association of Al-phyllsilicate and accompanying phases

Consistent with prior findings, we find that Al-phyllsilicate typically occurs stratigraphically above Fe/Mg-phyllsilicate across Mars in Nili Fossae, Libya Montes, Hellas Planitia, Terra Sirenum, and Mawrth Vallis. However, we find that the stratigraphy, mineralogic associations, and textures of the Al-phyllsilicates in these regions indicate that there are multiple processes producing the Al-phyllsilicates that differ by region. We identify two primary processes. In Hellas Planitia and the Eridania Basin portion of Terra Sirenum, the Al-phyllsilicate is best explained by pedogenic leaching of a basaltic protolith. In Nili Fossae, Libya Montes, eastern Terra Sirenum, and Valles Marineris, we find that the mineralogy is better explained by Al-phyllsilicate formation from a distinct protolith from that of the Fe/Mg-phyllsilicate, most likely a sedimentary or volcanoclastic material like an ash. In Mawrth Vallis, the stratigraphy is complex and could suggest a history of multiple Al-phyllsilicate formation processes, including alteration of basalt followed by emplacement and alteration of a distinct sedimentary/volcanoclastic protolith. Here we present our results on the phyllsilicate, jarosite, alunite, and Fe oxide geologic relationships and stratigraphic context. We discuss our interpretations of their formation mechanisms further in section 5.

4.3.1 Al-phyllsilicate formation from weathering sequences

4.3.1.1 Hellas Planitia

Consistent with prior findings (Carter et al., 2015), Al-phyllsilicate and Fe/Mg-phyllsilicate are abundant in the plains north of Hellas Planitia. These plains are largely Noachian sedimentary plains, as indicated by their fine layering (Salese et al., 2016). We detect Al-phyllsilicate in 27 images, largely in the sedimentary intercrater plains, though some deposits are in crater rims or sedimentary crater infill (Figure 5).

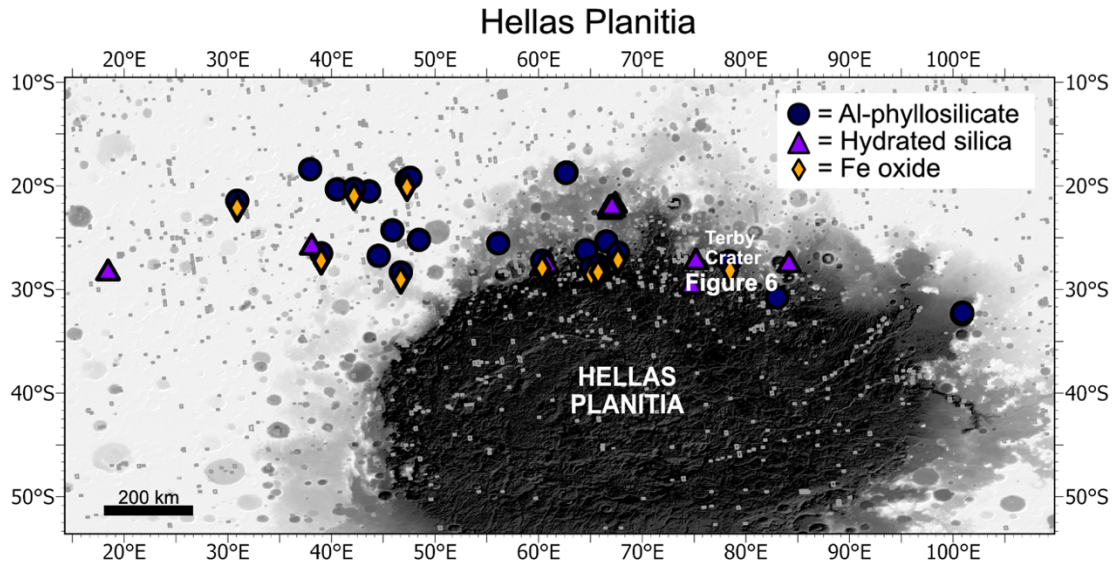


Figure 5: Distribution of detections of Al-phyllsilicate, hydrated silica, and Fe oxide (where it is detected in Al-phyllsilicate-bearing images) in Hellas Planitia within CRISM MTRDR images (footprints in gray). The location of subsequent Figure 6 is labeled. The basemap is the MOLA interpolated DEM (USGS).

The stratigraphic relationship between Al-phyllsilicate and Fe/Mg-phyllsilicate is best exemplified in image FRT00013D3A (Figure 6). This image is located in heavily eroded terrain to the west of the region and has previously been described by Carter et al. (2015). This image contains a mound of largely spectrally bland material with some weak hydration signatures. Within this mound, kaolinite is exposed overlying Fe/Mg-phyllsilicate (Figure 6b). The phyllsilicates appear to be part of the same geologic unit: they both exhibit a m-scale polygonally-fractured texture, and there is no sharp contact between these minerals (Figure 6c, d). While in this case there is no mixing of the phyllsilicates' spectral signatures at the CRISM resolution of 18 m/pixel, the HiRISE imagery indicates that there appears to be a gradational transition from one mineral to the other.

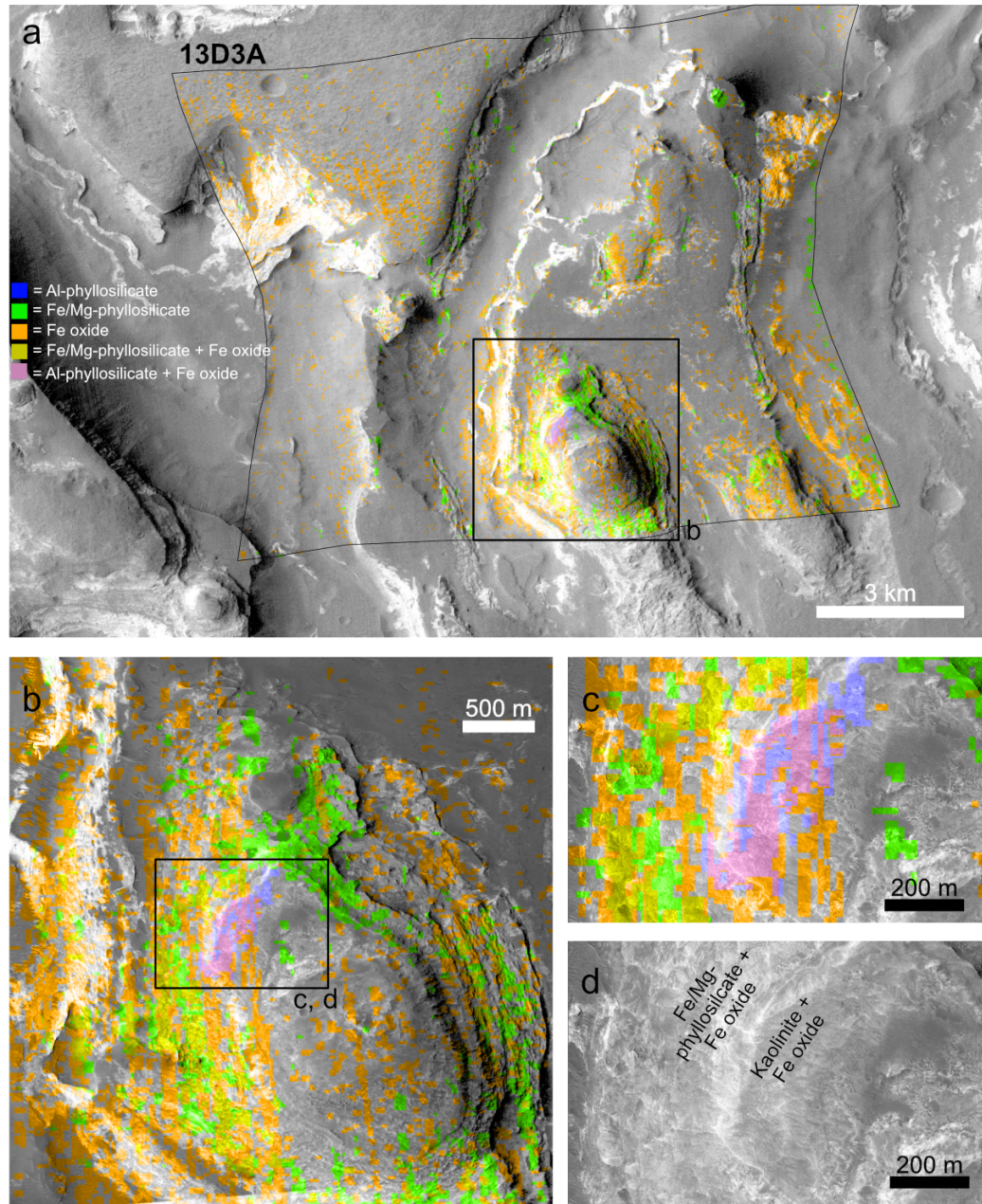


Figure 6: a) The full mineral map of image FRT00013D3A showing kaolinite, Fe/Mg-phylosilicate, and Fe oxide within layered deposits on the northern edge of Hellas Planitia. b) The central mound of this deposit showing Al-phylosilicate stratigraphically overlying Fe/Mg-phylosilicate, both mixed with Fe oxide. c, d) A close-up of the phyllosilicate stratigraphy showing that both phyllosilicates have similar fractured textures with a conformable, gradational transition between them.

Unlike the other Al-phylosilicate-bearing regions examined here, Hellas Planitia contains abundant Al-phylosilicate that is spectrally-mixed with Fe/Mg-phylosilicate at

the CRISM resolution of 18 m/pixel. This is demonstrated in image FRT0000643D (Figure 7). In this image, abundant Fe/Mg-phyllosilicate and a small deposit of Al-phyllosilicate are exposed in the intercrater plains of likely sedimentary origin (Salese et al., 2016). Much of the Al-phyllosilicate is spectrally-mixed with Fe/Mg-phyllosilicate, and there is no texture distinction between them at the available CTX resolution (5 m/pixel). Because these intercrater plains are thought to be sedimentary materials deposited by Noachian alluvial and/or lacustrine processes (Salese et al., 2016), it is possible that the Al- and Fe/Mg-phyllosilicates formed from aqueous alteration of a protolith that was then transported and deposited in these sedimentary plains, leading to the observed spectral mixing and textural similarity of these phyllosilicate units. While the influence of post-formation mixing cannot be entirely ruled out, a clear stratigraphic sequence of Al-phyllosilicate overlying Fe/Mg-phyllosilicate is preserved in e.g., image 13D3A (Figure 6), and the phyllosilicates in the plains are not completely mixed. Therefore, we conclude that the phyllosilicate formation and their resulting spectral mixing likely postdates most of the plains' deposition and reworking.

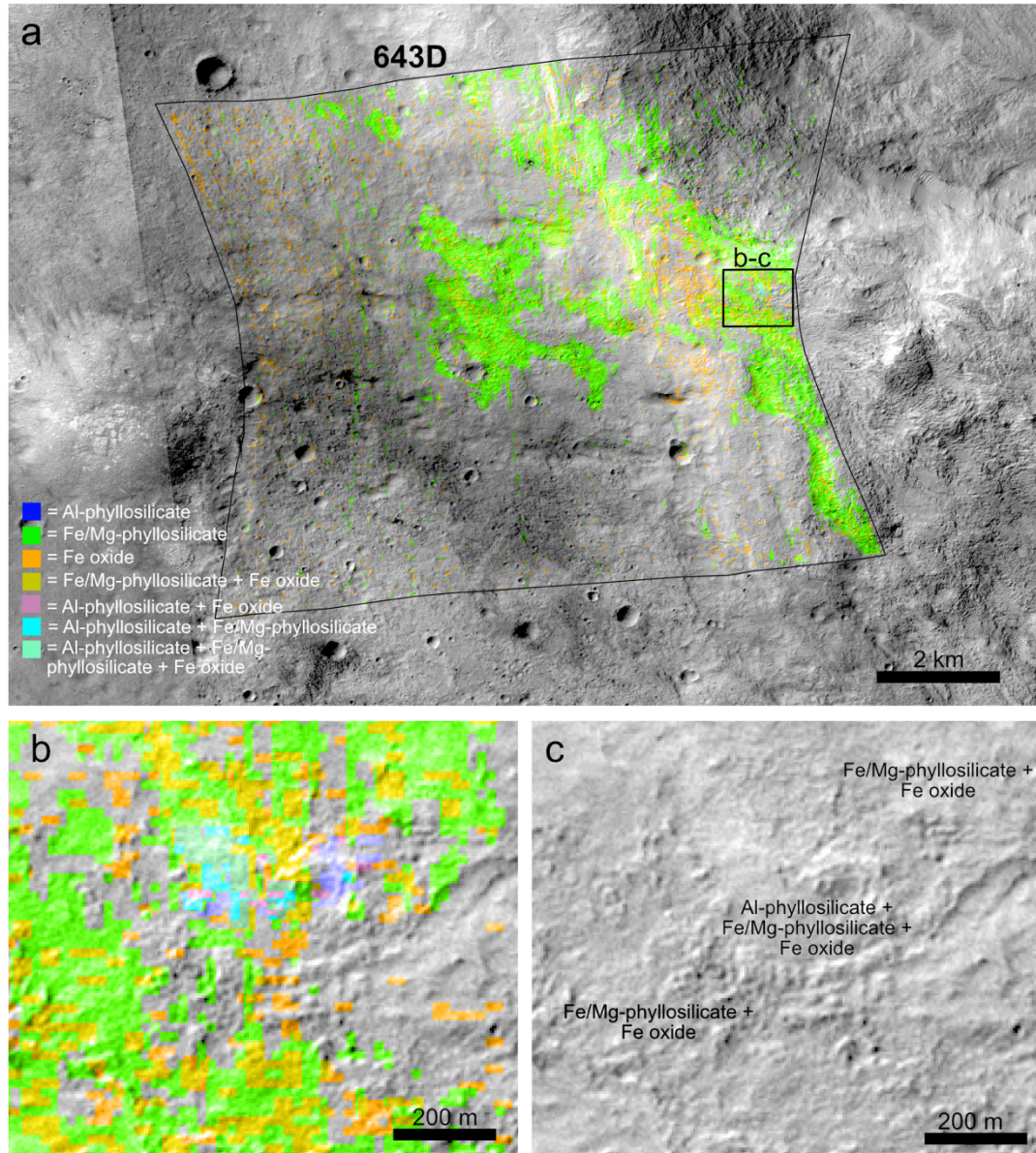


Figure 7: a) The full mineral map of image FRT000643D showing kaolinite, Fe/Mg-phyllsilicate, and Fe oxide within the sedimentary intercrater plains on the northern edge of Hellas Planitia. b, c) Close-up example of the Al-phyllsilicate, which is largely mixed with Fe/Mg-phyllsilicate and Fe oxide. At the available CTX resolution (5 m/pixel), the Al-phyllsilicate appears texturally indistinct from the Fe/Mg-phyllsilicate.

Fe oxide is frequently detected in mixtures with Al-phyllsilicate throughout the region. In particular, Al-phyllsilicate that is spectrally mixed with Fe/Mg-phyllsilicate also tends to be spectrally mixed with Fe oxide within those same geologic units. We detect Fe oxide mixed with both Fe/Mg-phyllsilicate and Al-phyllsilicate in 13D3A

(Figure 6c) and 643D (Figure 7b). Neither jarosite nor alunite were detected in this region.

4.3.1.2 Eridania Basin, western Terra Sirenum

We detect Al-phyllsilicate throughout Terra Sirenum, including in Eridania Basin in the western portion of the region (Figure 8). Like in Hellas Planitia, we observe that Al-phyllsilicate overlies Fe/Mg-phyllsilicate, and they are often spectrally mixed at the contact. These two phyllosilicates have similar textures and lack sharp unconformities between them. This indicates that there is a gradational transition between these minerals, which is consistent with the prior interpretation of their formation as part of a pedogenic leaching sequence (Noe Dobrea et al., 2008; Adeli et al., 2015; Pajola et al., 2016; Leask et al., 2024).

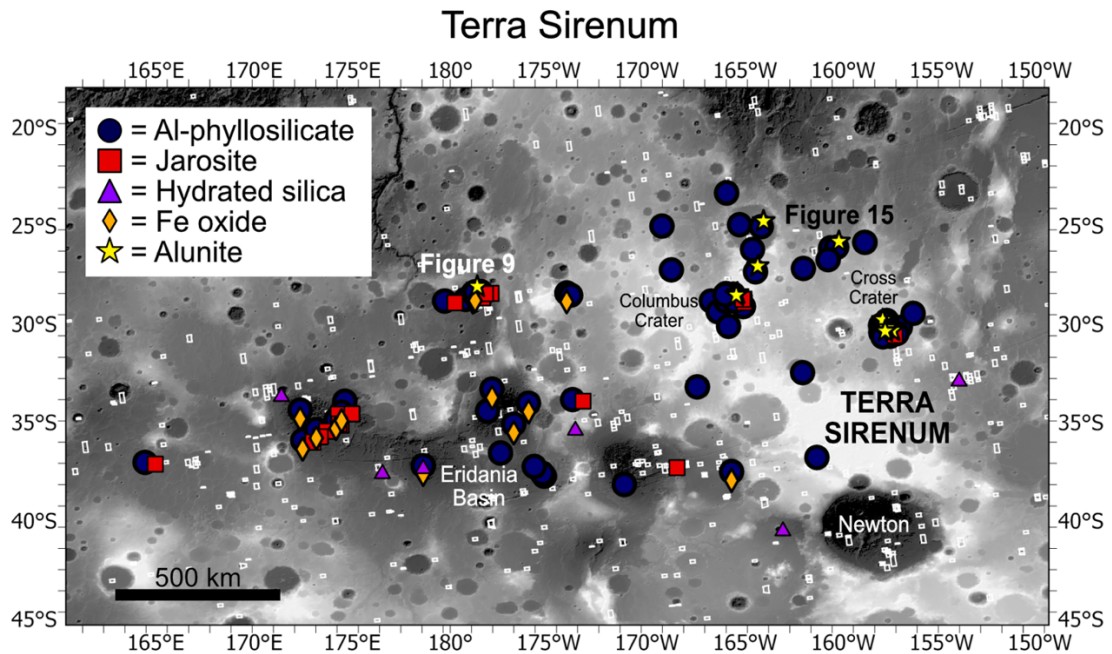


Figure 8: Distribution of detections of Al-phyllsilicate, hydrated silica, and Fe oxide (where it is detected in Al-phyllsilicate-bearing images) in Terra Sirenum within CRISM MTRDR images (footprints in gray). The locations of subsequent figures 9 and 15 are labeled. The basemap is the MOLA interpolated DEM (USGS).

The relationship between the Al-phyllsilicate and Fe/Mg-phyllsilicate is exemplified in image FRT00096FE. Here we observe Al-phyllsilicate, including Al-phyllsilicate mixed with jarosite, in contact with Fe/Mg-phyllsilicate (Figure 9). While the mixing of these minerals is not observed here at the CRISM spatial resolution, both the Al-phyllsilicate and the Fe/Mg-phyllsilicate have m-scale polygonal fractures and no sharp contact between them in HiRISE imagery (Figure 9b,c).

In this region, we corroborate prior detections of jarosite mixed with both Fe/Mg-phyllsilicate and Fe/Mg-phyllsilicate (Carter et al., 2015; Pajola et al., 2016; Leask et al., 2024; Hughes et al., 2024) as well as alunite mixed with Al-phyllsilicate (Leask et al., 2024). We also identify several new detections of jarosite associated with Fe/Mg-phyllsilicate, largely in the westernmost part of Eridania Basin (that which wraps around to being in the far eastern hemisphere of Mars). These sulfates largely appear to correlate to veins intersecting the phyllsilicates. Fe oxide is also commonly found in association with both Al-phyllsilicate and Fe/Mg-phyllsilicate in this region.

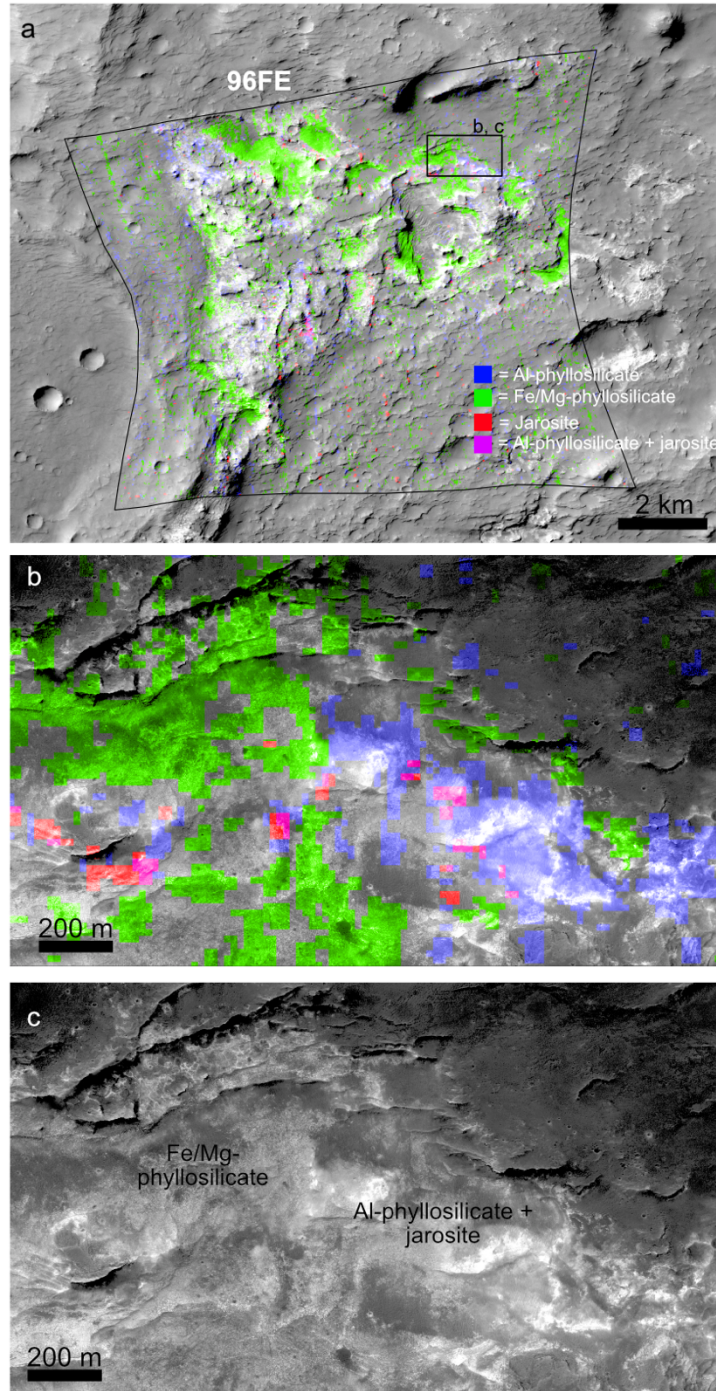


Figure 9: a) The full mineral map of the image FRT000096FE showing Al-phyllsilicate, Fe/Mg-phyllsilicate, and jarosite in light-toned deposits within Eridania Basin. b, c) A close-up of the phyllosilicate units. Al-phyllsilicate is mixed with sparse jarosite. Both Al-phyllsilicate and Fe/Mg-phyllsilicate have similar textures with m-scale polygonal fractures, and there is no sharp unconformable contact between them. Instead, there appears to be a conformable, gradational contact.

4.3.2 Al-phyllsilicate formation from volcanoclastic alteration

4.3.2.1 Nili Fossae

We identified 56 images that contain Al-phyllsilicate, most with multiple deposits or exposures. Based on the Gaussian fitting parameters and visual examination of the spectra, almost all Al-phyllsilicate in Nili Fossae is kaolinite with a few scattered detections of the two other distinctive aluminosilicates (Figure 2; Baker and Ehlmann, in review). Kaolinite is always associated with adjacent Fe/Mg-phyllsilicate. As reported previously (Ehlmann et al., 2009), kaolinite-rich terrain with accompanying Fe/Mg-phyllsilicate occurs around the fossae and Isidis impact basin, while hydrated silica (opal) primarily occurs on plains to the southwest along with Fe/Mg-phyllsilicate, illite and chlorite (Figure 10).

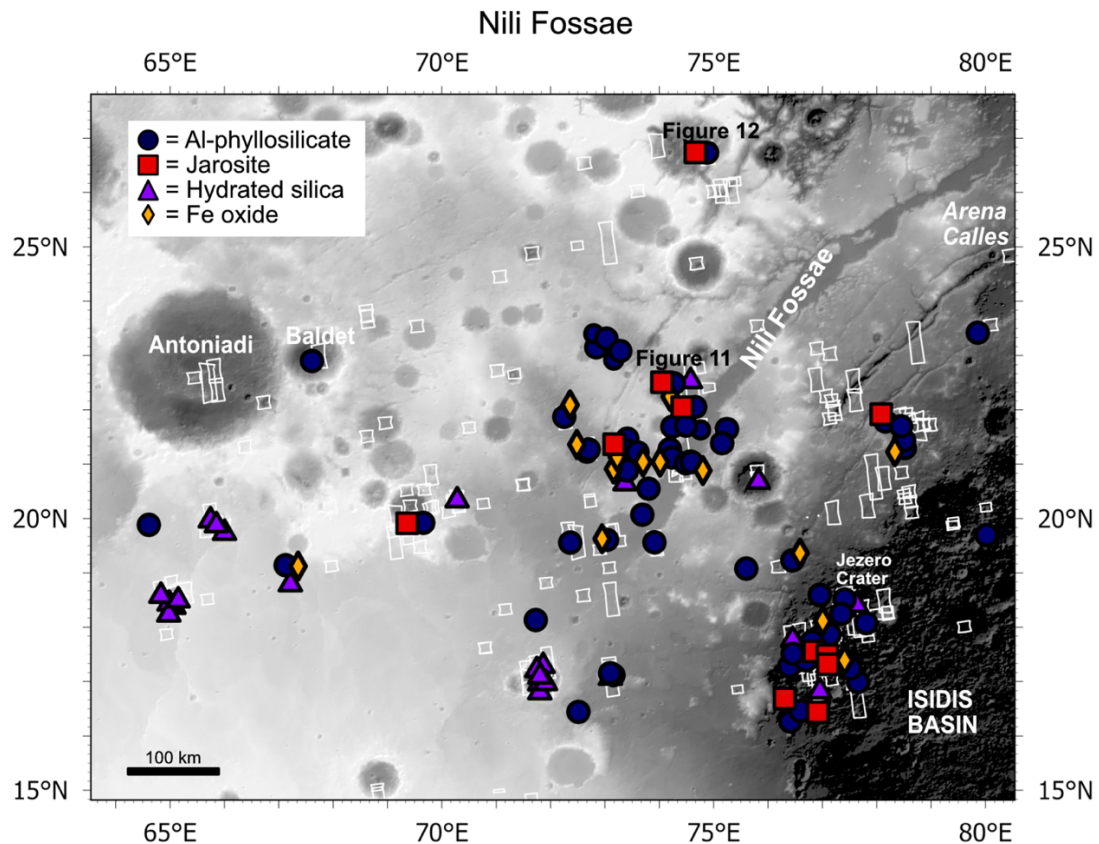


Figure 10: Distribution of detections of Al-phylllosilicate, jarosite, hydrated silica, and Fe oxide (where it is detected in Al-phylllosilicate-bearing images) in Nili Fossae within CRISM MTRDR images (footprints in white). The locations of subsequent figures 11 and 12 are labeled. The basemap is the MOLA interpolated DEM (USGS).

In agreement with prior findings (Ehlmann et al., 2009; Carter et al., 2015), the kaolinite in Nili Fossae consistently occurs stratigraphically above Fe/Mg-phylllosilicate. These two minerals are almost never mixed at the scale of a CRISM pixel (18 m). In several cases, the boundaries between the kaolinite and the Fe/Mg-phylllosilicate are sharp unconformities, and these minerals correspond to discrete textural units. Kaolinite typically appears as high-albedo patches with cm–m scale irregular fractures suggesting a friable material, sometimes exposed on the edges of flat, layered plateaus whose layering suggests sedimentary deposits, such as in image FRT0000A053 (Figure 11). Where there are clearer exposures such as in image HRL0000AB0A, the kaolinite units demonstrate m-scale layering that contacts the Fe/Mg-phylllosilicate unconformably (Figure 12). The Fe/Mg-phylllosilicate units mostly appear knobby, rough, and unlaminated, though some patches have similar polygonal fractures to the kaolinite.

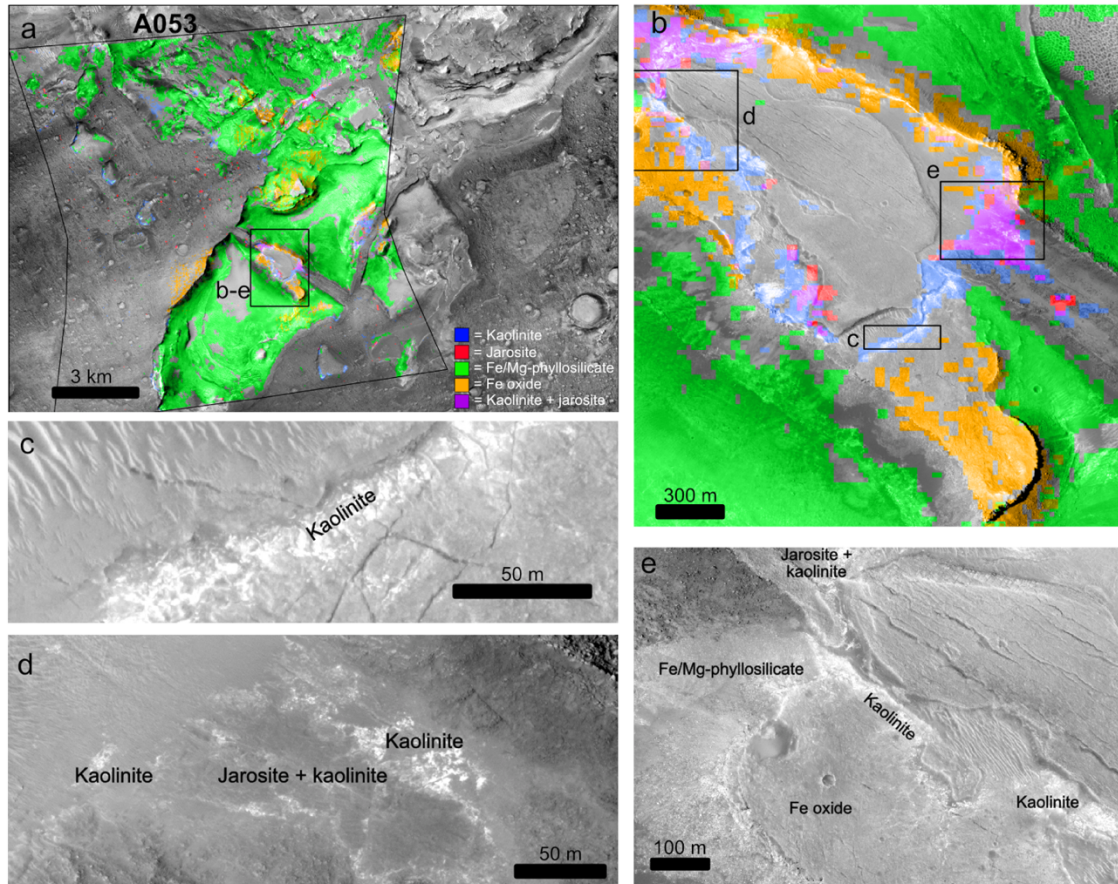


Figure 11: a) The full mineral map of FRT0000A053 showing Al-phyllsilicate, Fe/Mg-phyllsilicate, jarosite, and Fe oxide in crater sedimentary fill. A large aeolian-carved pit exposes several hundred m of Fe/Mg-phyllsilicate, with kaolinite and jarosite around the edges of two remnant plateaus. b) The central remnant plateau showing a bland capping unit overlying a kaolinite- and jarosite-bearing unit, overlying an Fe-oxide-bearing unit, overlying Fe/Mg-phyllsilicate. c) Kaolinite exposed in the edge of the plateau scarp face with m-scale polygonal fracturing distinct from the texture of the underlying spectrally-bland material. d) An example of the relationship between kaolinite and jarosite around the plateau. Here, smooth, darker-toned jarosite is mixed with and surrounded by light-toned kaolinite. e) A portion of the central plateau in demonstrating this multi-layered stratigraphy.

We identify five deposits of jarosite in Nili Fossae, all closely associated with Al-phyllsilicate. In some cases, such as in AB0A, the jarosite appears intimately mixed throughout the kaolinite (Figure 12b). In others, the strongest jarosite signal aligns with discrete darker-toned patches in contact with and mixed with lighter-toned kaolinite (e.g. in A053, Figure 11d). Fe oxide sometimes occurs within the same images as Al-

phyllosilicate in this region (Figure 10), but it is not found to be mixed with the Al-phyllosilicate and is instead observed on its own or mixed with Fe/Mg-phyllosilicate (Figure 11a). In A053, where Fe oxide occurs adjacent to kaolinite, it is not mixed with it but instead corresponds to a texturally distinct unit stratigraphically between the Al-phyllosilicate and the underlying Fe/Mg-phyllosilicate (Figure 11e).

For a more detailed examination of the Al-phyllosilicate and jarosite stratigraphy in Nili Fossae, see Baker and Ehlmann (in review).

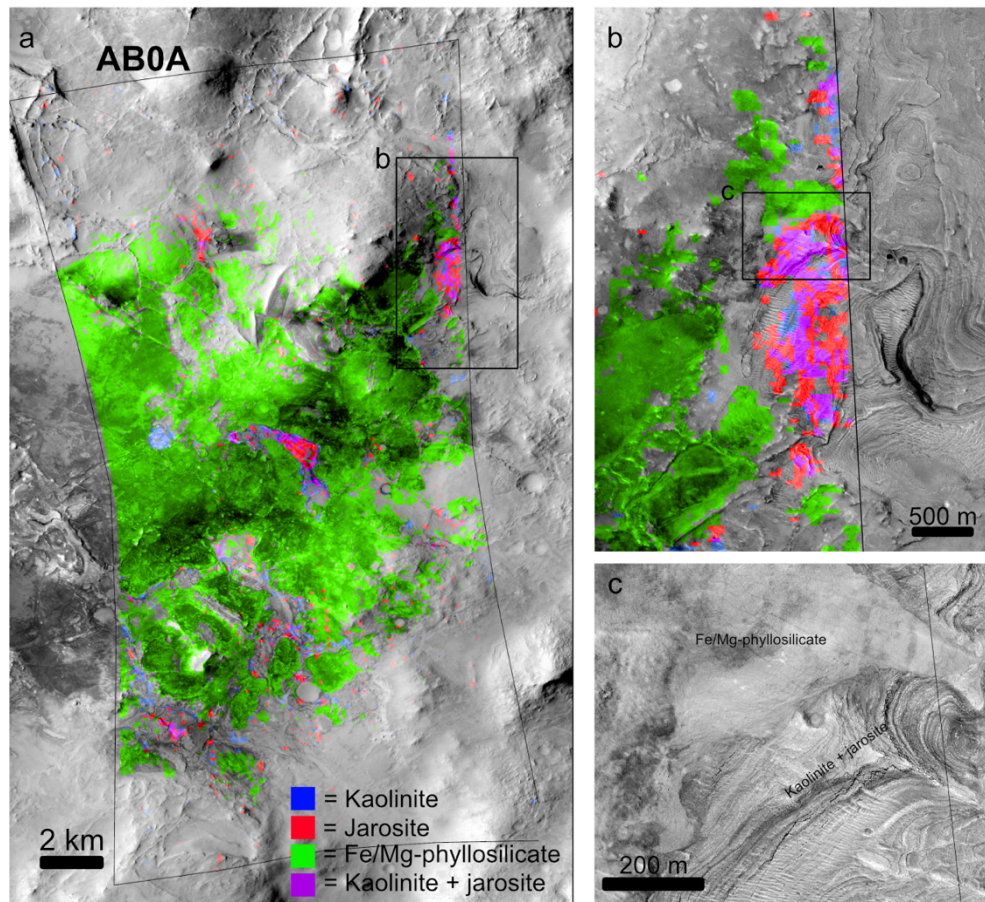


Figure 12: a) The full mineral map of HRL0000AB0A showing Al-phyllosilicate, Fe/Mg-phyllosilicate, and jarosite in crater sedimentary fill. b) The alteration mineralogy stratigraphy exposed by a canyon carved through this fill. The Fe/Mg-phyllosilicate unit is rough, knobby, and lacks visible layering. The jarosite and kaolinite are mixed in m-scale layers. c) The same stratigraphy at higher resolution

4.3.2.2 Libya Montes

While much of the region is obscured by dust coverage, Libya Montes contains 7 images with exposed Al-phyllsilicate (Figure 13). These Al-phyllsilicate deposits occur in distinct stratigraphic units from the more widespread Fe/Mg-phyllsilicate in this region. No jarosite or alunite is detected in this region. Sparse Fe oxide is detected, but we do not observe it associated with or mixed with Al-phyllsilicate.

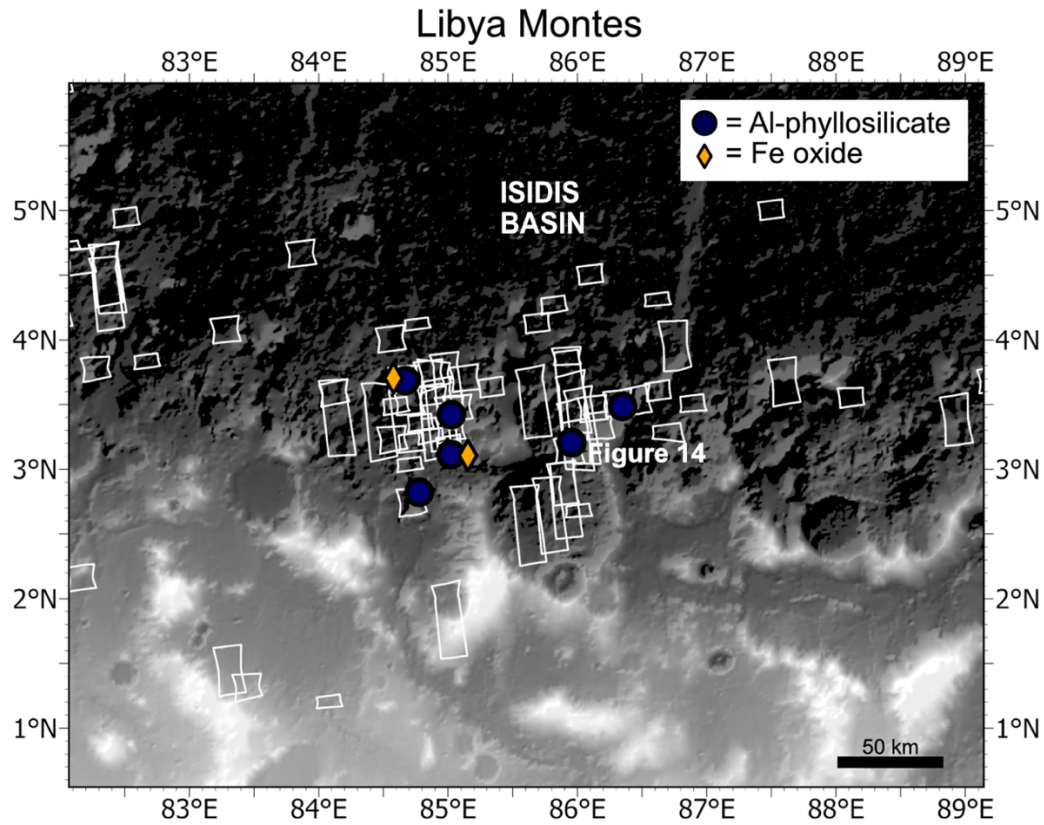


Figure 13: Distribution of detections of Al-phyllsilicate and Fe oxide (where it is detected in Al-phyllsilicate-bearing images) in Libya Montes within CRISM MTRDR images (footprints in white). The location of subsequent figure 14 is labeled. The basemap is the MOLA interpolated DEM (USGS).

We observe Al-phyllsilicate in two primary contexts: eroding out of blocks exposed in crater floors and a channel wall, and in layered sedimentary deposits. These blocks have been previously interpreted to be Noachian massifs that likely pre-date and were disrupted by the Isidis impact (Bishop et al., 2013), so it is challenging to interpret the original phyllsilicate stratigraphy. However, there is no observable mixing of Al-

phyllosilicate and Fe/Mg-phyllosilicate, and they appear to occur in distinct geologic units. In present-day Libya Montes, these blocks are exposed in crater and channel walls and floors and so have likely been even further disrupted. We observe similar these Al-phyllosilicate-bearing blocks in four of the seven Al-phyllosilicate-bearing images in this region.

The Al-phyllosilicate in sedimentary deposits such as in image FRT000B0CB preserve stratigraphic context (Figure 14). This image is taken of an outflow channel that flows into Isidis basin from a ~62 km impact crater. Al-phyllosilicate, namely montmorillonite and kaolinite, is exposed around the edges of a layered plateau in the neck of the channel (Figure 14b). The Al-phyllosilicate is in light-toned deposits with m-scale polygonal fractures and layers (Figure 14c,d), very similar to the kaolinite deposits observed in Nili Fossae (Figure 11). Sparse Fe/Mg-phyllosilicate is exposed nearby in the crater wall, but it is not detected alongside Al-phyllosilicate in these layered sedimentary deposits.

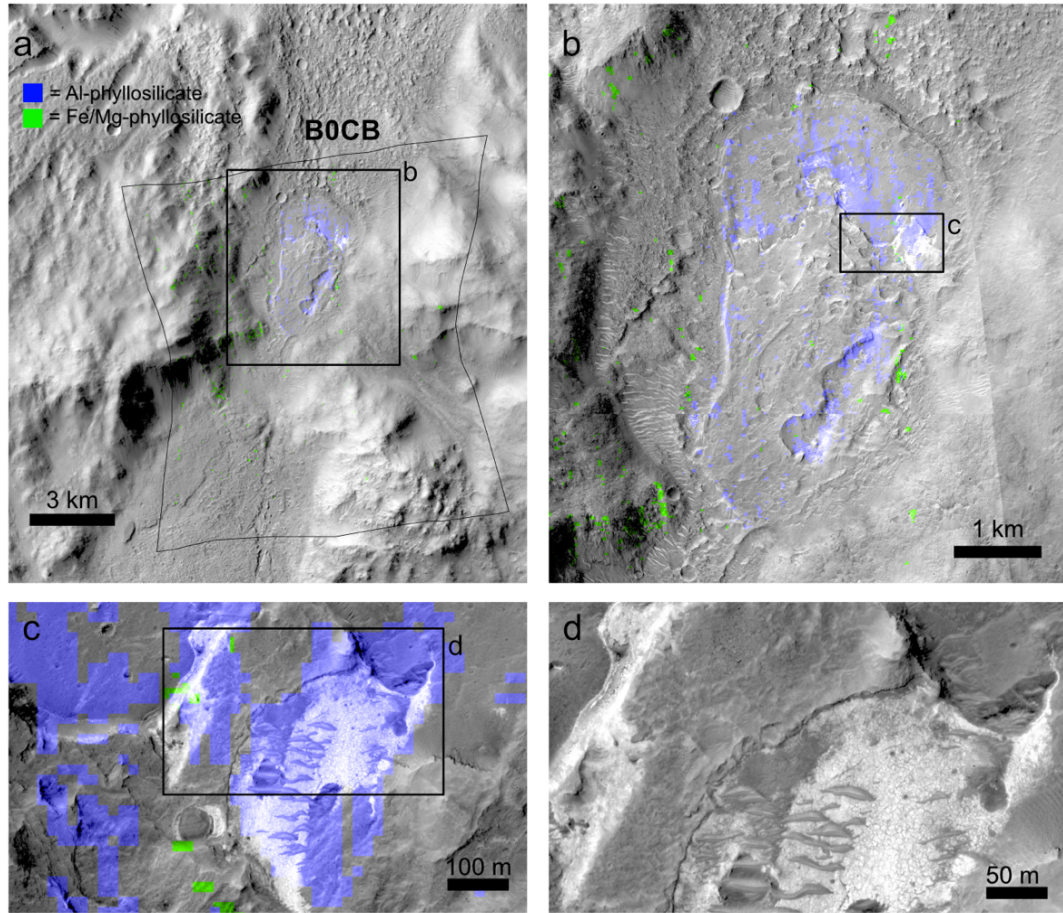


Figure 14: a) The full mineral map of the image FRT000B0CB showing Al-phyllsilicate and Fe/Mg-phyllsilicate in a layered deposit in the neck of an impact crater outflow channel. b) Al-phyllsilicate on the edges and within exposed layers of this deposit. c) Close-up example showing the association of Al-phyllsilicate with light-toned units within the layered deposit. d) Close-up example of the polygonally-fractured and/or layered textures of the Al-phyllsilicate.

4.3.2.3 Terra Sirenum

Here we exclude Eridania Basin, where the Al-phyllsilicate stratigraphy appears distinct from the rest of the region (see section 4.3.1.2) and focus on the impact craters and intercrater plains in the eastern portion of Terra Sirenum. In this region, we detect Al-phyllsilicate in 37 images. Fe/Mg-phyllsilicate exposures at the surface are sparse in this region, but it likely exists at depth as indicated by its exposure in crater ejecta (Leask et al., 2024). Almost all Al-phyllsilicate in eastern Terra Sirenum is found in

impact craters, concentrated in Columbus and Cross Craters as has been described by Wray et al. (2011), Ehlmann et al. (2016), and Leask et al. (2024). Only four of 37 images containing Al-phylosilicate occur in the intercrater plains (Figure 8).

Much of the Al-phylosilicate, which is dominantly kaolinite, is found in m-scale layers in this region. These deposits increase in thickness towards the neighboring volcano Arsia Mons (Leask et al., 2024). This layered kaolinite is demonstrated in image HRL000132BC in a ~40 km substantially infilled crater in the northeast of the region (Figure 15). In this image, Fe/Mg-phylosilicate is exposed in smooth material in the crater wall. Several deposits of Al-phylosilicate are exposed throughout the crater floor in infilled material. Some of this Al-phylosilicate corresponds to small light-toned mounds carved out of this material, and some is found in m-scale layered infill deposits. In this image, we observe a small amount of alunite mixed with the Al-phylosilicate in the layered deposits (Figure 15b).

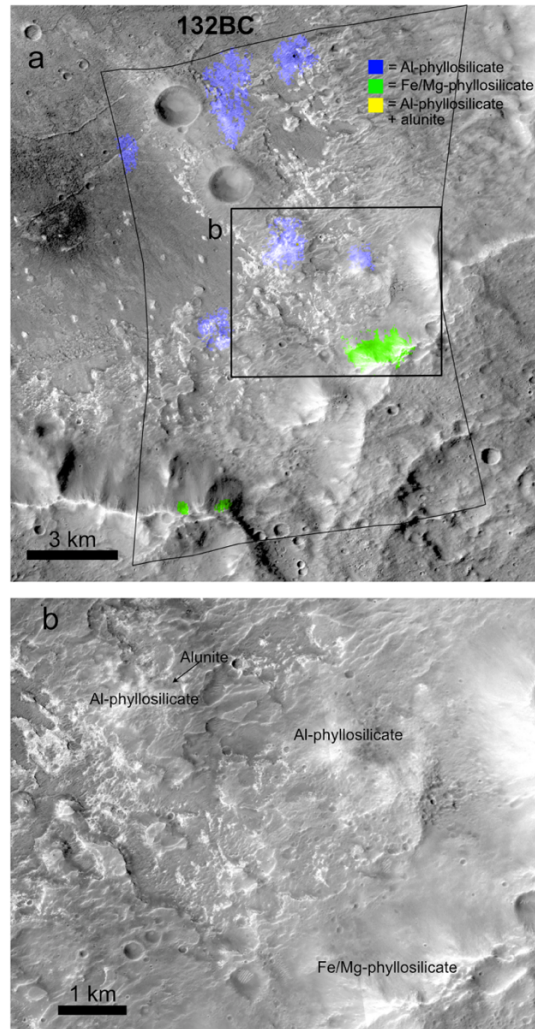


Figure 15: a) The full mineral map of the image HRL000132BC showing Al-phyllsilicate, Fe/Mg-phyllsilicate and a small deposit of alunite within infill material in an impact crater. b) Close-up example showing the Fe/Mg-phyllsilicate exposed in the crater wall, while Al-phyllsilicate and alunite are found in crater floor deposits. Al-phyllsilicate is observed in both light-toned mounds and in finely layered deposits.

In this region, we observe jarosite mixed with Al-phyllsilicate in Cross Crater and Columbus Crater. Both craters have complex histories with possible lacustrine periods and local volcanism, so they may not be representative of wider regional processes (Wray et al., 2011; Ehlmann et al., 2016).

Both jarosite and alunite are detected in association with Al-phyllsilicate in eastern Terra Sirenum. Jarosite is not associated with Fe/Mg-phyllsilicate in this region,

unlike in Eridania Basin. Fe oxide is not observed alongside Al-phyllsilicate in eastern Terra Sirenum.

4.3.2.4 Valles Marineris

Al-phyllsilicate is abundant in Valles Marineris, primarily exposed in the walls of the chasms (Figure 16). It is less commonly associated with Fe/Mg-phyllsilicate than in other regions of Mars. Throughout the region, particularly in Ius Chasma, Melas Chasma, and Coprates Chasma, we observe Al-phyllsilicate exposed in the chasm walls on the edge of thin, light-toned deposits or in a smooth layer that appears to be draped over underlying topography. This draping stratigraphy is exemplified in image FRT0000AD3D (Figure 17), where there is a shallow scarp between the Al-phyllsilicate-bearing layer and the underlying spectrally bland terrain (Figure 17b,c). This region also contains extensive hydrated silica in similar geologic units (Figure 8e). Fe/Mg-phyllsilicate is not observed nearby these Al-phyllsilicate deposits.

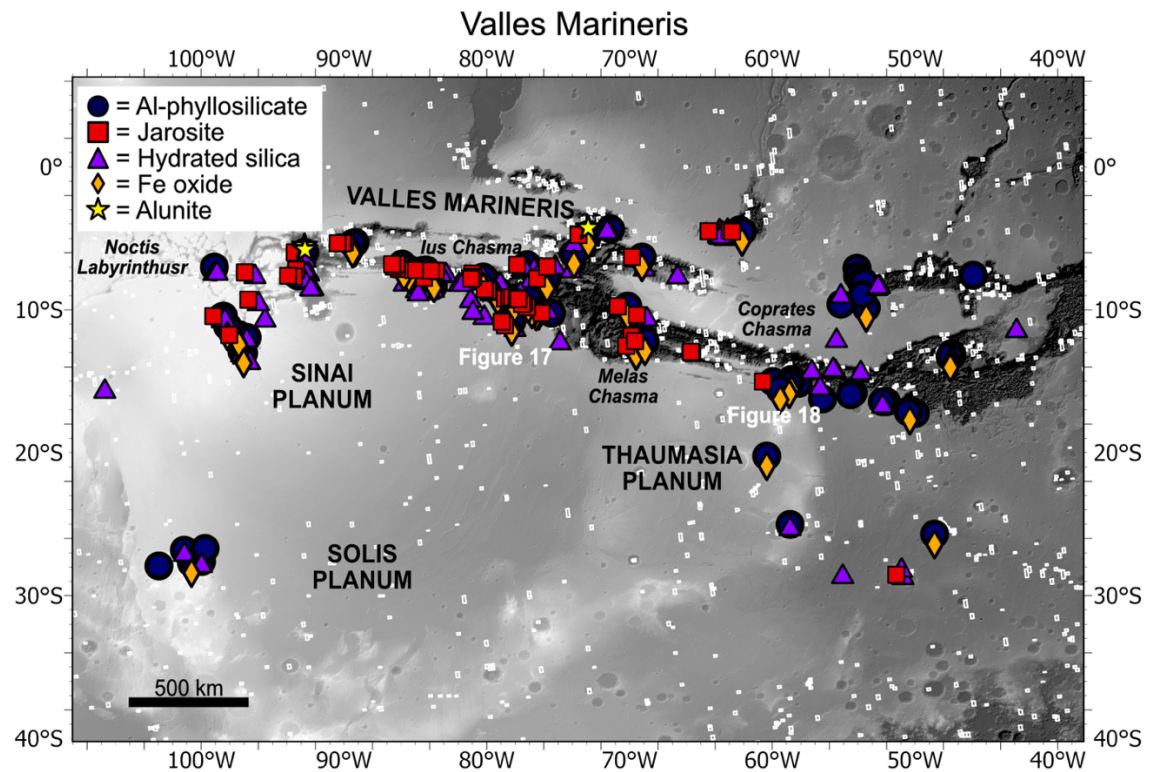


Figure 16: Distribution of detections of Al-phyllsilicate, jarosite, alunite, hydrated silica, and Fe oxide (where it is detected in Al-phyllsilicate-bearing images) in Valles

Marineris within CRISM MTRDR images (footprints in white). The locations of subsequent figures 17 and 18 are labeled. The basemap is the MOLA interpolated DEM (USGS).

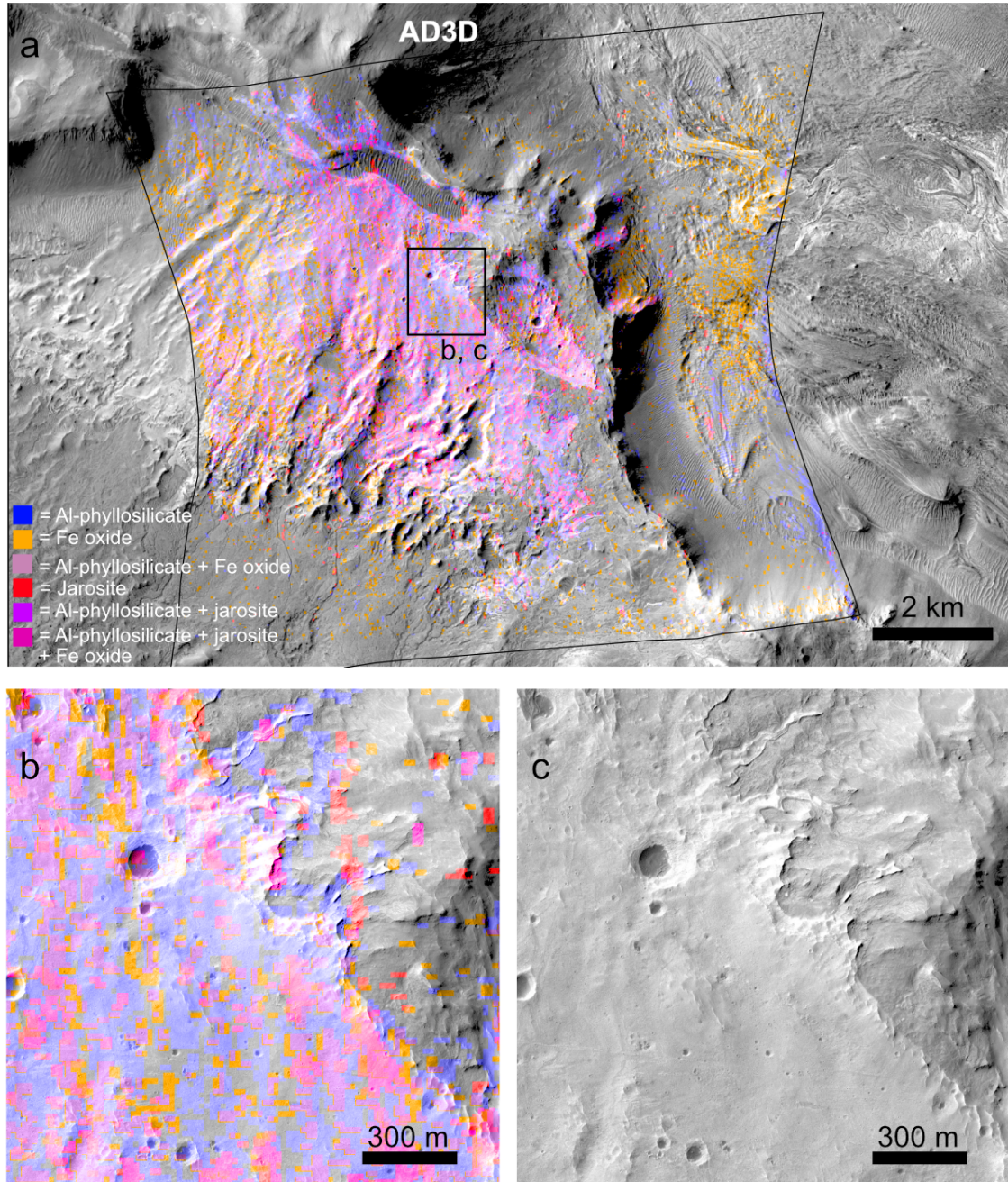


Figure 17: a) The full mineral map of the image FRT000AD3D showing Al-phyllsilicate, jarosite, and Fe oxide within Ius Chasma b, c) Al-phyllsilicate, jarosite, and Fe oxide are well-mixed in a smoother layer that apparently drapes the underlying

topography, as shown by the contact between this unit and the underlying spectrally-bland material.

In Coprates Chasma in eastern Valles Marineris, Al-phyllsilicate is exposed alongside Fe/Mg-phyllsilicates. The Al-phyllsilicate, largely kaolinite in this region, occurs stratigraphically above the Fe/Mg-phyllsilicate. This stratigraphy is demonstrated in FRT0000B6C5 (Figure 18). In this image, the two minerals differ in texture, with the Al-phyllsilicate corresponding to light-toned units with m-scale roughness, while the Fe/Mg-phyllsilicate units are smoother. In some locations, there appears to be a sharp contact between them, indicating an unconformity (Figure 18b). Where this contact is exposed on steep topographic relief, there is a margin where the spectral signatures of both minerals are detectable in the CRISM spectra, and there appears to be a textural gradient from one phyllsilicate to the other (Figure 18c). At the available resolution, we cannot discriminate between this mixed zone being caused by a gradational transition between minerals or by physical mixing due to mass wasting. Because this gradient is observed on steep slopes, and the contact is sharp elsewhere, we judge that mass wasting mixing is a more likely explanation.

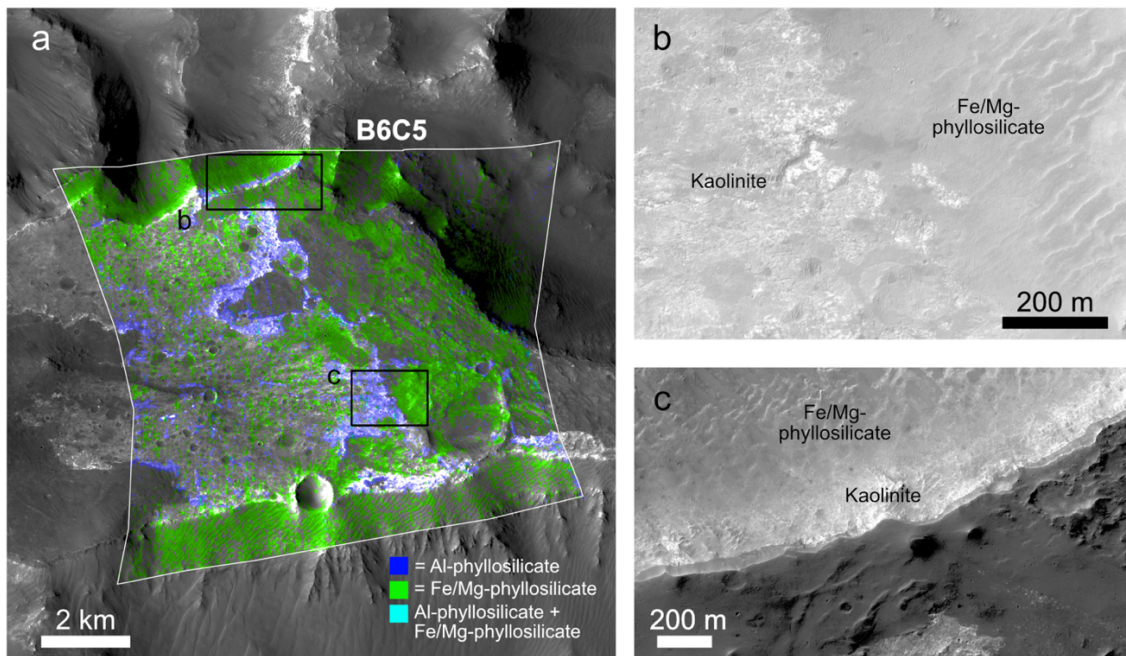


Figure 18: a) The full mineral map of the image FRT000B6C5 showing Al-phyllsilicate and Fe/Mg-phyllsilicate in a plateau and chasm walls within Coprates Chasma. b) Close-up example of the contact between Al-phyllsilicate—kaolinite in this case— and Fe/Mg-phyllsilicate. The kaolinite unit is light-toned with m-scale polygonal fractures, and the Fe/Mg—phyllsilicate unit is smooth. There is a sharp contact between these units. c) Close-up of the contact between kaolinite and Fe/Mg-phyllsilicate on a steep chasm wall. There may be a gradational transition from one mineral to the other, but it is difficult to distinguish that from the effects of mixing due to mass wasting on this steep slope.

In agreement with prior findings (Weitz et al., 2011; Thollot et al., 2012), we find Al-phyllsilicate stratigraphically underlying Fe/Mg-phyllsilicate in Noctis Labyrinthus. We also note image FRT00011DF2 in Coprates Chasma, where we observe Al-phyllsilicate mixed with jarosite overlying Fe/Mg-phyllsilicate but also observe a small deposit of Al-phyllsilicate seemingly underlying the Fe/Mg-phyllsilicate.

Jarosite and Fe oxide are abundant throughout Valles Marineris. In western Valles Marineris, these minerals are frequently mixed with Al-phyllsilicate and hydrated silica in the thin layer draping underlying topography. In this region, these three alteration minerals appear intimately mixed (e.g. Figure 17). Three images were found to contain alunite: we corroborated detections of alunite in FRT0000A48D and FRT00009180 (Viviano et al., 2013) and found a new detection in FR0000A86A (Figure 16). These alunite deposits are observed mixed with Al-phyllsilicate and hydrated silica in images that also contain jarosite, and all were found within the interior of the chasms. There is an evident positive correlation between jarosite-alunite and Fe oxide occurring preferentially alongside Al-phyllsilicate deposits that are deeper in the interior of the chasms. In eastern Valles Marineris, where Al-phyllsilicate is primarily observed at higher elevations on plateaus or the plains surrounding the chasms, jarosite and Fe oxide are sparser, and the Al-phyllsilicate typically lacks these associated alteration phases (Figure 16).

4.3.2.5 Mawrth Vallis

The nature of the phyllsilicate stratigraphy in Mawrth Vallis has been much examined and much debated since hyperspectral imagery of it was first acquired. Our

analysis of this region is also ambiguous, but it appears that multiple Al-phylllosilicate formation processes may have been present over its long alteration history, as we observe characteristics that appear consistent with both the Al-phylllosilicate stratigraphy we observe in Hellas Planitia/Eridania Basin and that which we observe in Nili Fossae/Libya Montes/Terra Sirenum/Valles Marineris.

We detect abundant Al-phylllosilicate throughout this region, primarily on the intercrater plains adjacent to the Mawrth Vallis channel (Figure 19). Out of 85 images, we detect jarosite in 8 images. The jarosite appears to occupy two distinct units: on its own without other detectable phases stratigraphically above the Al-phylllosilicate (as discussed in Farrand et al., (2009, 2014)), and mixed with Al-phylllosilicate (the “doublet phase” discussed by Bishop et al. (2020) that we attribute to mixed Al-phylllosilicate + jarosite). We detect alunite in four images, all mixed with Al-phylllosilicate. Fe oxide is frequently detected mixed with Al-phylllosilicate and Fe/Mg-phylllosilicate throughout the region.

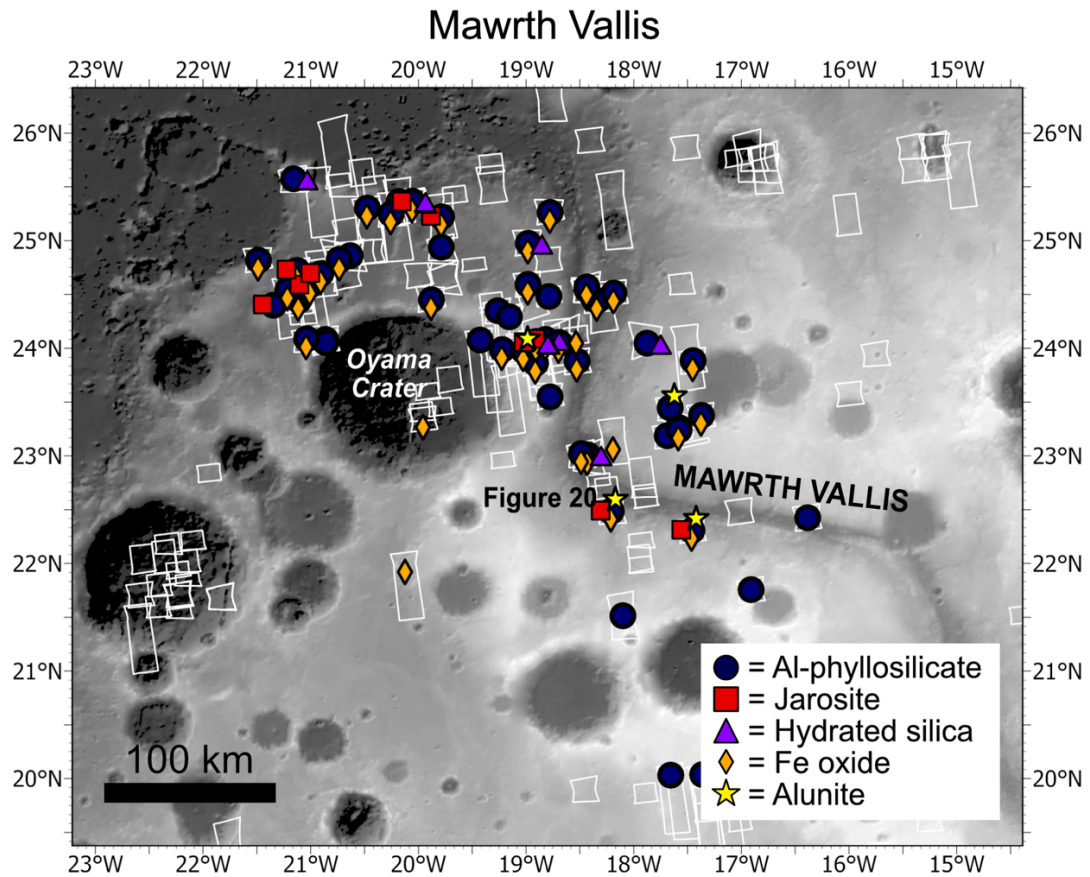


Figure 19: Distribution of detections of Al-phyllsilicate, jarosite, hydrated silica, and Fe oxide (where it is detected in Al-phyllsilicate-bearing images) in Mawrth Vallis within CRISM MTRDR images (footprints in white). The location of subsequent figure 20 is labeled. The basemap is the MOLA interpolated DEM (USGS).

The complex Al-phyllsilicate mineralogy is exemplified in image FRT00003BFB. This image is located on the slopes adjacent to the Mawrth Vallis valley and is bisected by a younger side channel (Figure 20a). In this image, we observe Al-phyllsilicate in a light toned unit stratigraphically overlying Fe/Mg-phyllsilicate. Fe oxide occurs on its own without other detectable phases, but we also detect it mixed with both Al-phyllsilicate and Fe/Mg-phyllsilicate. We detect jarosite and alunite mixed with the Al-phyllsilicate. The alunite is mixed throughout the Al-phyllsilicate, but there appears to be an association with jarosite occurring on the edges of the Al-phyllsilicate where it contacts spectrally bland material. This bland material may indicate sand accumulation in local topographic lows, which jarosite exposed on the

edges of these lows (Figure 20b). The contact between the Al-phyllsilicate and Fe/Mg-phyllsilicate is sharp along parts of the contact, with a clear color difference between the minerals. The Al-phyllsilicate has m-scale polygonal fractures, and the texture of the Fe/Mg-phyllsilicate varies from smooth to a similar polygonally fractured texture. Along portions of the contact, the transition from one phyllsilicate to the other appears more gradational, though a clear color difference between them remains (Figure 20c).

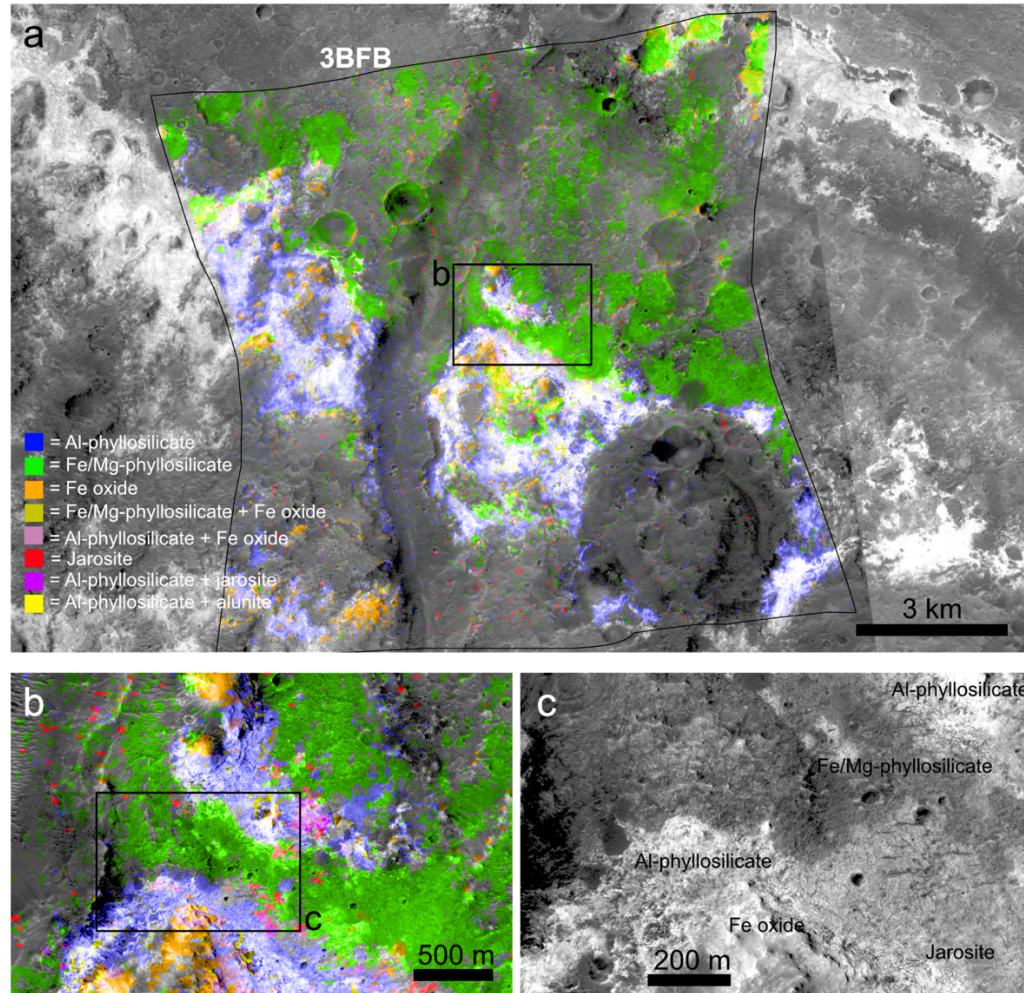


Figure 20: a) The full mineral map of image FRT0003BFB showing Al-phyllsilicate, Fe/Mg-phyllsilicate, jarosite, alunite, and Fe oxide on a slope adjacent to Mawrth Vallis. b) Close-up of the distribution of these alteration minerals. Al-phyllsilicate overlies Fe/Mg-phyllsilicate. Fe oxide overlies Al-phyllsilicate and mixes with it at the contact. Jarosite is mixed with Al-phyllsilicate largely near the contact with Fe/Mg-phyllsilicate. c) Close-up demonstrating the textures and contacts of these minerals. The Al-phyllsilicate unit is light toned with m-scale polygonal fractures, and the Fe/Mg-phyllsilicate is darker toned but with a similar texture.

5 Discussion

5.1 Formation of Al-phyllsilicate and associated minerals

5.1.1 Al-phyllsilicate formation as part of a pedogenic leaching sequence

If Al-phyllsilicate formed as part of a pedogenic leaching sequence from basalt as has been proposed for the regions examined here (e.g. Noe Dobrea et al., 2008; Ehlmann et al., 2009; Loizeau et al., 2010; Carter et al., 2015), we would expect to see a conformable relationship between the Al-phyllsilicate overlying Fe/Mg-phyllsilicate. These minerals would likely have similar textures, and where the contact between them is exposed, we would expect a gradational transition from one to each other, possibly with mixed spectra visible at the CRISM scale (18m/pixel). This is consistent with terrestrial laterites, where there are often several meters of mixing between the Al-phyllsilicate and Fe/Mg-phyllsilicate-bearing zones (Gaudin et al., 2005; Gaudin et al., 2011) that may be visible at CRISM's resolution depending on the geometry of the exposure. Additionally, if this pedogenic leaching occurred under oxidizing and neutral pH conditions, Fe oxides would be expected to form alongside the phyllsilicates (Nesbitt and Young, 1989; Gaudin et al., 2005; Greenberger et al., 2012; Blesa and Maroto, 1986). Under very acidic or reducing conditions, iron could be mobile and be transported out of the deposit.

Of the six regions we examined, Al phyllsilicate formation by basalt weathering is the most consistent process for our observations of the Al-phyllsilicate stratigraphy at Hellas Planitia and Eridania Basin in western Terra Sirenum. In Hellas Planitia, Al-phyllsilicate and Fe/Mg-phyllsilicate are frequently mixed at the CRISM resolution of 18 m/pixel. Where these minerals occur in the same image, the two phyllsilicates typically have similar textures (Figure 6, 7) and lack sharp contacts. This textural similarity and spectral mixing indicate that they formed from the same protolith, consistent with the conclusions of Carter et al. (2015).

As expected for leaching of basalt under oxidizing conditions (Nesbitt and Young, 1989; Gaudin et al., 2005; Greenberger et al., 2012; Blesa and Maroto, 1986), Fe oxide is

found alongside much of the Al- and Fe/Mg-phyllosilicate in Hellas Planitia and Eridania Basin. In Hellas Planitia, we observe Fe oxide apparently intimately mixed throughout the Al-phyllosilicate to Fe/Mg-phyllosilicate weathering sequence exposed in 13D3A, as well as elsewhere in the image where it occurs on its own not mixed with any other detectable phases (Figure 6). We do not detect any jarosite or alunite in this region, which suggests that the alteration occurred under more neutral pH conditions. In Eridania Basin, we detect sparse alunite alongside Al-phyllosilicate and jarosite alongside both Al-phyllosilicate and Fe/Mg-phyllosilicate. This indicates a period of acidic alteration, either the original alteration of basalt to form these phyllosilicates or a later period of acidic fluid interaction.

In contrast to Hellas Planitia and Eridania Basin where we conclude that pedogenic leaching of basalt most likely formed the Al-phyllosilicate, the Al-phyllosilicate in these other regions appears more predominantly kaolinite rather than montmorillonite. Kaolinite can form from the aqueous alteration of volcanic ashes in well-drained landscapes where base cations are able to be flushed from the system (Wilson, 2004; Wada, 1987).

5.1.2 Al-phyllosilicate and jarosite-alunite formation from silicic volcanoclastic deposits

5.1.2.1 Formation of Al-phyllosilicate and Fe/Mg-phyllosilicate from distinct protoliths

In the other regions of Mars that we examined here, the Al-phyllosilicate does not appear to be consistent with formation from a basaltic protolith as part of a leaching sequence. In Nili Fossae, Libya Montes, eastern Terra Sirenum, and Valles Marineris, the Al-phyllosilicate is better explained by formation from alteration of a volcanoclastic material like an ash.

In these regions, where Al-phyllosilicate and Fe/Mg-phyllosilicate occur adjacent to each other, they correspond coherently to units with distinct textures. In Nili Fossae, Libya Montes, and Terra Sirenum, Al-phyllosilicate is often layered or exposed in sedimentary plateaus that are consistent with formation from a transported sedimentary material (Figure 11, 12, 14, 15). In contrast, the Fe/Mg-phyllosilicate in these regions is unlayered. In Valles Marineris, much of the Al-phyllosilicate occurs in a unit that

appears to be draped over the underlying topography and lacks exposed associated Fe/Mg-phyllosilicate (Figure 17). Where the contact between these minerals is exposed, there is no mixing, and it appears unconformable. This is consistent with formation of the Al- and Fe/Mg-phyllosilicates from two distinct protoliths.

We conclude that the best match for the Al-phyllosilicate stratigraphy in these regions is formation through alteration of a pyroclastic deposit such as volcanic ash. Whereas sediments would be similar to the underlying stratigraphy, ash provides the difference in protolith. This ash was likely deposited regionally as an airfall deposit which, depending on local conditions, then either sintered in place as a layer draped over underlying topography or was reworked by aeolian and/or water-driven erosion and transport to accumulate in local sedimentary basins. This deposition was followed by syn- or post-depositional Al-phyllosilicate formation from aqueous alteration. The ash layer was largely deposited on top of a basaltic unit that had previously weathered into Fe/Mg-phyllosilicate or weathered into Fe/Mg-phyllosilicate during the alteration of the ash to Al-phyllosilicate. In this formation scenario, the Al-phyllosilicate in layered deposits in sedimentary basins including in Nili Fossae, Libya Montes, and Terra Sirenum likely represent alteration of reworked ash, while the Al-phyllosilicate in a layer that appears draped over the topography in Valles Marineris likely formed through alteration of a direct airfall deposit.

We find a diversity of Al-phyllosilicate compositions within and between regions examined here (Figure 1, 2). While most regions contain both kaolinite and montmorillonite as well as other aluminosilicate compositions, we find that for these regions whose Al-phyllosilicate formation we attribute to pedogenic leaching, their compositions tend towards a predominance of montmorillonite over kaolinite. We observe this in Hellas Planitia (Figure 1d) as well as in Mawrth Vallis, which may have had leaching (see Section 5.1.3) (Figure 1g). Terra Sirenum appears dominantly kaolinite in its scatterplot, but we note that this plot includes all of Terra Sirenum beyond Eridania Basin. The Al-phyllosilicate in Eridania Basin specifically tends toward montmorillonite compositions. Formation of montmorillonite over kaolinite indicates poor drainage in the system, allowing the concentration of base cations (Wilson, 2004; Clark et al., 2007).

Under previous interpretations of Al-phyllsilicate formation from pedogenic leaching of basalt across Mars, these Al-phyllsilicates represent an extensive amount of aqueous alteration, perhaps the most altered material on the planet (Wilson, 2004; Price et al., 2005; Carter et al., 2015). If the Al-phyllsilicate protolith is instead an Al/Si-rich volcanic ash, less cumulative contact with water is likely required to produce the observed Al-phyllsilicate. This is due to the initially higher concentration of Al in the protolith and because ashes are glassy and porous and therefore weather rapidly (Aomine and Wada, 1962; Stefánsson and Gíslason, 2001; Ugolini and Dahlgren, 2002; Ye and Michalski, 2021). Indeed, an order of magnitude less cumulative weathering may be necessary, equating to an upper limit of several million years of aqueous activity in these regions (Bishop et al., 2018; Wilson and Head, 1994; Baker and Ehlmann, in review).

5.1.2.2 Formation of jarosite–alunite and Fe oxide from volcanic ash

Formation of these Al-phyllsilicates from a volcanic ash protolith is also supported by their association with jarosite and alunite. Jarosite is found to be mixed with Al-phyllsilicate/hydrated silica in Nili Fossae, Terra Sirenum, Valles Marineris, and Mawrth Vallis. Crucially, we do not detect jarosite mixed with Fe/Mg-phyllsilicate in these regions.

The conditions necessary to form jarosite are: sufficient Fe and S, pH of 1.5–4.5 (Symonds et al., 1994; Poulet et al., 2009; Ehlmann et al., 2016), and oxidizing conditions. To form alunite, low pH is required alongside sufficient Al^{3+} (Symonds et al., 1994). Therefore, if there was widespread regional circulation of acidic fluids, we would expect this acidic alteration to form jarosite in association with Fe-phyllsilicates (supplying the requisite Fe), while alunite would form in association with Al-phyllsilicates (supplying the requisite Al). It is therefore surprising that in these regions, jarosite is almost always associated with Al-phyllsilicate and never with Fe/Mg-phyllsilicate. This suggests that the conditions necessary to form jarosite are met in conjunction with the Al-phyllsilicate in these regions but not with the Fe/Mg-phyllsilicate. We argue that if the Al-phyllsilicate protolith, which is distinct from the Fe/Mg-phyllsilicate protolith in these regions, was S-bearing, the observed jarosite

could be produced through interaction of this protolith with Fe-bearing water. A geochemically distinct, S-bearing, aluminous sedimentary Al-phyllsilicate protolith is most consistent with a volcanic ash. Because Fe is required to form jarosite and the Al-phyllsilicate units in these regions largely lack other Fe-bearing minerals, we propose that Fe-enriched fluid could be produced by leaching Fe out of the Fe/Mg-phyllsilicate that underlies the Al-phyllsilicate in these regions. When this Fe-bearing water interacts with the S-bearing Al-phyllsilicate protolith, jarosite can precipitate. Alunite may have formed where the water interacting with the volcanic ash was less Fe-enriched, and the local Al combined with local S to produce alunite.

In these regions where we propose that Al-phyllsilicate formed from a volcanic ash, Fe oxide is typically not mixed with the Al-phyllsilicate unless jarosite is also present. This is consistent with our conclusion that the ash protolith was most likely aluminous with a low initial Fe content, and so where later Fe-bearing water did not interact with this material, no Fe minerals formed. In Valles Marineris and parts of Mawrth Vallis, Fe oxide is detected with Al-phyllsilicate where it is mixed with jarosite (Figure 16, 17, 19, 20). In Nili Fossae, and Terra Sirenum, we do not detect Fe oxide alongside Al-phyllsilicate + jarosite. This is likely due to differences in the timing of water interaction with these regions. Jarosite is a metastable phase, and with continued contact with water, it will dissolve and reprecipitate as Fe oxides/hydroxides including goethite and hematite (Zolotov and Shock, 2005). Therefore, our observations of preserved jarosite without accompanying Fe oxides suggests that in these regions, jarosite formed during the final stages of significant water interaction. Where there is substantial Fe oxide alongside jarosite, there was likely continued aqueous alteration after the formation of jarosite.

5.1.3 Mawrth Vallis, a special multi-process case?

Unlike the other regions examined here, the mineralogy and stratigraphy observed in Mawrth Vallis does not appear to be consistent with either Al-phyllsilicate formation solely through pedogenic leaching of basalt or solely through alteration of an aluminous volcanic ash, but rather has elements consistent with both. As expected with formation as

a pedogenic leaching sequence under oxidizing conditions, we find that much of the Al-phyllsilicate in Mawrth Vallis is mixed with Fe oxide (Figure 19). Additionally, in some locations, the texture of Al-phyllsilicate is similar to that of the underlying Fe/Mg-phyllsilicate, and the contacts between them appear possibly gradational. However, in other locations, there do appear to be sharper contacts between the Al- and Fe/Mg-phyllsilicates, more consistent with formation from two distinct protoliths (Figure 20c).

Like in Nili Fossae, Valles Marineris, and eastern Terra Sirenum, we observe jarosite and alunite only mixed with Al-phyllsilicate, not Fe/Mg-phyllsilicate. This suggests a distinct Al-phyllsilicate chemistry, which is consistent with our ash hypothesis. In image 3BFB, jarosite appears to be preferentially exposed on the edges of local topographic lows, which could suggest its formation from ponding of late-stage fluid as has been proposed (Michalski et al., 2013; Bishop et al., 2020).

Because we observe elements consistent with both formation theories, we propose that both could have influenced the formation of Al-phyllsilicate in Mawrth Vallis. Bishop et al. (2008) find that the Al-phyllsilicate in this region is composed of two distinct units, a kaolinite unit overlying a montmorillonite unit. This compositional diversity may be consistent with our proposed formational diversity, as we find a possible association of montmorillonite predominance with regions of basaltic leaching and kaolinite predominance with volcanic ash alteration. Klidas et al. (2025) find that the true thicknesses of the Al-phyllsilicate units in Mawrth Vallis are consistent with draping over the landscape, either from top-down pedogenic leaching or an airfall deposit. Both could have produced the observed geometry.

5.2 Implications of Al-phyllsilicate formation from ash for Mars' volcanism

If many of the Al-phyllsilicate-bearing regions formed from a volcanic ash as we propose, some of the possible volcanic sources are clear while others are ambiguous. There is no clear evidence for volcanoes in Nili Fossae or Libya Montes, but ash could have been sourced from the large adjacent Syrtis Major volcano (Kerber et al., 2013; Fawdon et al., 2015; Robbins et al., 2011). Additionally, fissure volcanism can lack an easily detectable geomorphic signature at the surface but could be the source of these

pyroclastics. Ash deposits are expected to be thicker at closer distances to their source volcanoes. In Nili Fossae, few Al-phyllsilicate deposits could be measured, but there is no clear directional pattern in the measured apparent thicknesses that indicates the volcanic source (Baker and Ehlmann, in review). This may indicate the effects of post-depositional reworking of the ash to accumulate in topographic lows. In Terra Sirenum, the apparent thicknesses of the Al-phyllsilicate thin with increasing distance from the volcano Arsia Mons, which suggest that that volcano is its volcanic source (Leask et al., 2024). In Mawrth Vallis, the thickness of the Al-phyllsilicate does not increase monotonically in a direction that points to its source, but the measured thicknesses do indicate that it is in a unit that is draped across the underlying topography in the region, consistent with an airfall deposit (Klidas et al., 2025).

If Al-phyllsilicate in Nili Fossae, Libya Montes, Terra Sirenum, Valles Marineris, and Mawrth Vallis all formed through alteration of Al/Si-rich volcanic ash as we contend, this suggests a more widespread record of explosive volcanism and evolved compositions than previously thought. Mars has had extensive volcanism, but the geologic evidence points to largely effusive rather than explosive behavior (Greeley and Spudis, 1981; Hauber et al., 2010). Explosive volcanism is expected to be common on Mars (Baker, 2001; Wilson, 2009), so this prevalence of effusive as opposed to explosive volcanism has been an open question in Mars geology.

Much of the potential evidence for explosive volcanism is easily eroded and so would not be expected to survive long term in the geologic record (Zimbelman et al., 2015). However, the analysis of Al-phyllsilicate and our interpretation that a large number of the deposits are best explained by an ash protolith may provide a new, better-preserved source of evidence for the extent of explosive volcanism in Mars's past that suggests it is more extensive than previously indicated by fragile geomorphic indicators.

Our analysis of Al-phyllsilicate formation also suggests that these ash deposits are more evolved than basaltic or otherwise mafic compositions. Mars is dominantly mafic in composition (e.g. Christensen et al., 2000; McSween, 2009), though a growing body of research suggests the presence of localized evolved (i.e., more felsic) compositions (e.g., Christensen et al., 2005; Wray et al., 2013; Rogers and Farrand, 2022; Phillips et al., 2022). These evolved rocks, which are widespread on Earth, form through

either subduction zone dynamics or fractional crystallization in a magma chamber. While Mars was not thought to have plate tectonics, fractional crystallization appears to be a distinct possibility to produce evolved lavas (Udry et al., 2018; Pieterek et al., 2026). Periods of silicic lava production would be expected to produce more explosive eruptions (Fink and Manley; 1989; Castro et al., 2014) which could have delivered the Al/Si-rich volcanoclastic Al-phylllosilicate protolith across Mars.

6 Conclusions

Our observations confirm that while Al-phylllosilicate is widespread across Mars, there is complexity and diversity between these Al-phylllosilicate-bearing regions. This diversity is present in their Al-phylllosilicate composition, in the composition of their accompanying alteration phases, and in their stratigraphy.

We conclude that our observations are most consistent with Al-phylllosilicate formation from two distinct processes across Mars. In northern Hellas Planitia and the Eridania Basin region of Terra Sirenum, we find that Al-phylllosilicate and the underlying Fe/Mg-phylllosilicate have similar textures. These textures vary with location from m-scale polygonal fractures to layers to smoother units, but the phylllosilicates are texturally similar to each other wherever they occur in these regions. Fe oxide is frequently mixed with both Al- and Fe/Mg-phylllosilicate, and jarosite and/or alunite is detected alongside both phylllosilicates in Eridania, though these sulfates are absent from Hellas Planitia. We conclude that these results are most consistent with the formation of Al-phylllosilicate from a pedogenic leaching sequence from a single basaltic protolith under oxidizing conditions.

In contrast, our observations of Al-phylllosilicate elsewhere on Mars do not appear to be consistent with formation from pedogenic leaching of basalt. In Nili Fossae, Libya Montes, eastern Terra Sirenum, and Valles Marineris, Al-phylllosilicate appears to be distinct from Fe/Mg-phylllosilicate. These units differ in texture, and where their contact is exposed, it tends to be sharp and unconformable. Where jarosite and alunite occur in these regions, they are strongly spatially associated with Al-phylllosilicate and never associated with Fe/Mg-phylllosilicate. Most Al-phylllosilicate in these regions lacks

associated Fe oxide with the exception of Valles Marineris, where continued alteration may have caused reprecipitation of jarosite as Fe oxide. The Al-phyllsilicate stratigraphy in Mawrth Vallis has elements consistent with both proposed formation processes, and we conclude that it most likely represents the combined effects of both processes operating in the region at different times.

We interpret the Al-phyllsilicate and jarosite–alunite in these non-pedogenic leaching regions to have formed from aqueous alteration of an aluminous volcanoclastic material like an ash. This ash was emplaced as an airfall deposit, some of which sintered in place and some of which was likely reworked and deposited in topographic lows such as impact craters. We conclude that jarosite and alunite likely formed within the Al-phyllsilicate protolith from alteration contemporaneously with or after Al-phyllsilicate formation. In this formation mechanism, the requisite S to produce the jarosite–alunite was likely sourced from the ash protolith from adsorbed sulfurous phases.

These results suggest that the extensive aqueous alteration required to produce Al-phyllsilicate from a basaltic protolith likely was not widespread across Mars. Instead, it was concentrated in only a small number of locations. Elsewhere, Al-phyllsilicate could have formed with an order of magnitude less cumulative contact with water. The Al-phyllsilicate units we interpret to have formed from aluminous ash also suggest more widespread explosive and evolved volcanism than previously thought.

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Open Research

All data from CRISM, CTX, HRSC, and THEMIS are freely available from the NASA through the Planetary Data System (<https://pds.nasa.gov/>). Data from HiRISE is available from the University of Arizona (<https://www.uahirise.org/>). Data from MOLA is

available from the United States Geological Survey (https://astrogeology.usgs.gov/search/map/mars_mgs_mola_dem_463m). Laboratory spectra from the USGS spectral library are available from the United States Geological Survey (<https://www.usgs.gov/labs/spectroscopy-lab/usgs-spectral-library>), and laboratory spectra from Brown University's RELAB spectral library are available from the NASA Planetary Data System (<https://pds-specplib.rsl.wustl.edu/search.aspx?catalog=RELAB>). Figures for this paper were generated with Python 3.8 and ArcGIS Pro.

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