

Chapter 2

ALUMINUM PHYLLOSILICATE AND JAROSITE FORMATION
THROUGH ALTERATION OF REWORKED AL/SI-RICH
VOLCANICLASTIC SEDIMENTS IN NILI FOSSAE, MARS

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Abstract

Aluminum-phyllsilicates occur in 1s–10s of km² exposures of Noachian (~3.7 Ga) rock across Mars. Al-phyllsilicates typically appear stratigraphically above Fe/Mg-phyllsilicates, and these units have been proposed to represent pedogenic basalt weathering sequences. In several regions, Al-phyllsilicates are spatially associated with jarosite and alunite, sulfate minerals indicative of strongly acidic waters. We examine Al-phyllsilicates in the Nili Fossae region, combining mineral maps generated from imaging spectroscopy with digital elevation models and high-resolution imagery to understand their geologic context and formation. We find that Al-phyllsilicate is dominantly kaolinite. Kaolinite-bearing units lack associated Fe oxide and typically have a distinct texture relative to Fe/Mg-phyllsilicate units, indicating an unconformity and that they did not form as part of a weathering sequence but rather from two different protoliths. Layers in some kaolinite deposits and their preferential association with sedimentary basins suggest that reworked sedimentary material is the protolith, most likely an Al/Si-enriched (non-basaltic) airfall volcanic deposit. We detect sparse jarosite closely associated with kaolinite which we interpret to have formed from the interaction of Fe-enriched fluids with S in the kaolinite protolith, subsequently discharged into an oxidizing atmosphere. These observations suggest less intense near-surface weathering than the basalt pedogenesis hypothesis, namely, an upper bound of several million cumulative years of aqueous activity in Nili Fossae that largely ended after the formation of jarosite. Detection of Al-phyllsilicate-bearing float rocks in nearby Jezero Crater by the Perseverance Rover shows that sample return has potential to conclusively determine processes and environmental conditions forming Nili Fossae's distinctive Al-phyllsilicates.

Plain language summary

Clay (phyllsilicate) minerals are produced by water interaction with silicate rocks, and so their detection across Mars is an indicator of the planet's history of water. Starting with basalt, the most common rock on Mars, iron/magnesium-clays form first from water

interaction followed by aluminum-clays after more extensive weathering. We examine Al-clay deposits in the Nili Fossae region. Corroborating prior findings, we determine that Al-clay consistently occurs overlying Fe/Mg-clay as expected if both minerals formed from basalt weathering. However, we find that these two minerals have distinct textures that indicate that they formed from different starting rocks deposited at different times. Layers in some Al-clay and its association with areas where sediments would accumulate suggest that this mineral formed from deposits of transported sediment rich in Al and Si; the most likely source is a volcanic deposit like an ash. No Fe oxide was detected alongside Al-phyllsilicate, but some jarosite was. Jarosite is an Fe sulfate that forms in oxidizing and highly acidic conditions. Shallow, iron-bearing groundwaters may have interacted with sulfur in the ash deposits. The deposits indicate several million cumulative years of water activity in the region with an oxidizing atmosphere and local acidic conditions.

1 Introduction

Extensive hydrated phyllosilicate (clay) minerals have been detected across Mars' surface by the infrared spectrometers OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité) and CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) on board the Mars Express orbiter and the Mars Reconnaissance Orbiter, respectively (Poulet et al., 2005; Mustard et al., 2008). Fe/Mg-phyllsilicates, typically smectites with some chlorites and serpentines, have been detected across the planet's surface, indicating widespread aqueous alteration. Al-phyllsilicates have also been detected and are the infrared spectrally dominant mineral in small 1–10s km² exposures of Noachian bedrock in a few select regions (Figure 1).

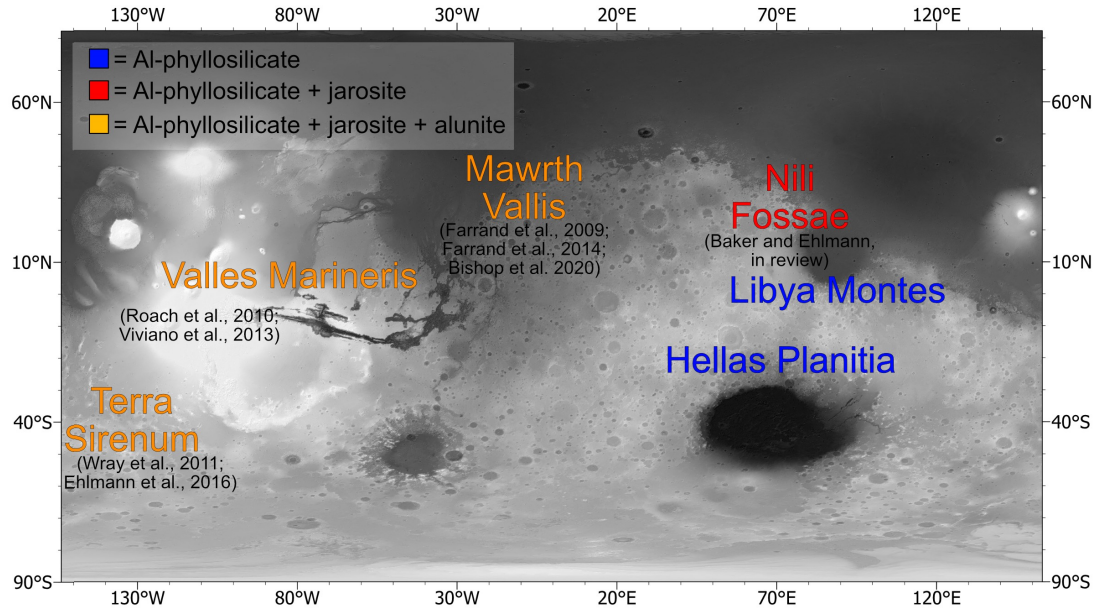


Figure 1: Global map of the six regions that contain Al-phyllsilicate-bearing units that appear to stratigraphically overlie Fe/Mg-phyllsilicate-bearing units (Carter et al., 2015). Colored circles indicate regions where nearby jarosite and/or alunite has been detected alongside Al-phyllsilicate.

These Al-phyllsilicates, 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 often been interpreted to be indicative of a high degree of alteration (e.g. Poulet et al., 2005; Mustard et al., 2008; Bishop et al., 2008; Ehlmann et al., 2009; Le Deit et al., 2012; Carter et al., 2015). If the initial rock before alteration is basalt—the most common rock type on Mars (McSween, 2009)—, then Fe/Mg-phyllsilicates are the thermodynamically favored first phases to form during aqueous alteration followed by Al-phyllsilicate (Chevrier et al., 2007; Velde and Meunier, 2008; Catalano, 2013). Where geologic units with Al-phyllsilicate occur on Mars, they are typically seen stratigraphically overlying units with Fe/Mg-phyllsilicate. Figure 1 indicates locations where this stratigraphy is observed: Nili Fossae (Poulet et al., 2005; Ehlmann et al., 2009), Mawrth Vallis (Poulet et al., 2005; Loizeau et al., 2007; Michalski and Noe Dobrea, 2007; Bishop et al., 2008; Wray et al., 2008), Valles Marineris (Murchie et al., 2009; Le Deit et al., 2012), Hellas Planitia (Carter et al., 2015), Terra Sirenum (Noe Dobrea et al., 2008), and Libya Montes (Bishop et al., 2013). As more-weathered material appears to overlie less-weathered material,

these regions have been interpreted as vertical weathering sequences, showing pedogenic leaching of the protolith as water propagates through the ground (e.g., Ehlmann et al., 2009, Michalski et al., 2013; Carter et al. 2015). Alternatively, Al-phyllsilicate could form overlying Fe/Mg-phyllsilicate from two distinct protoliths that are in contact rather than as a weathering sequence. Figure 2 illustrates these endmember alteration scenarios.

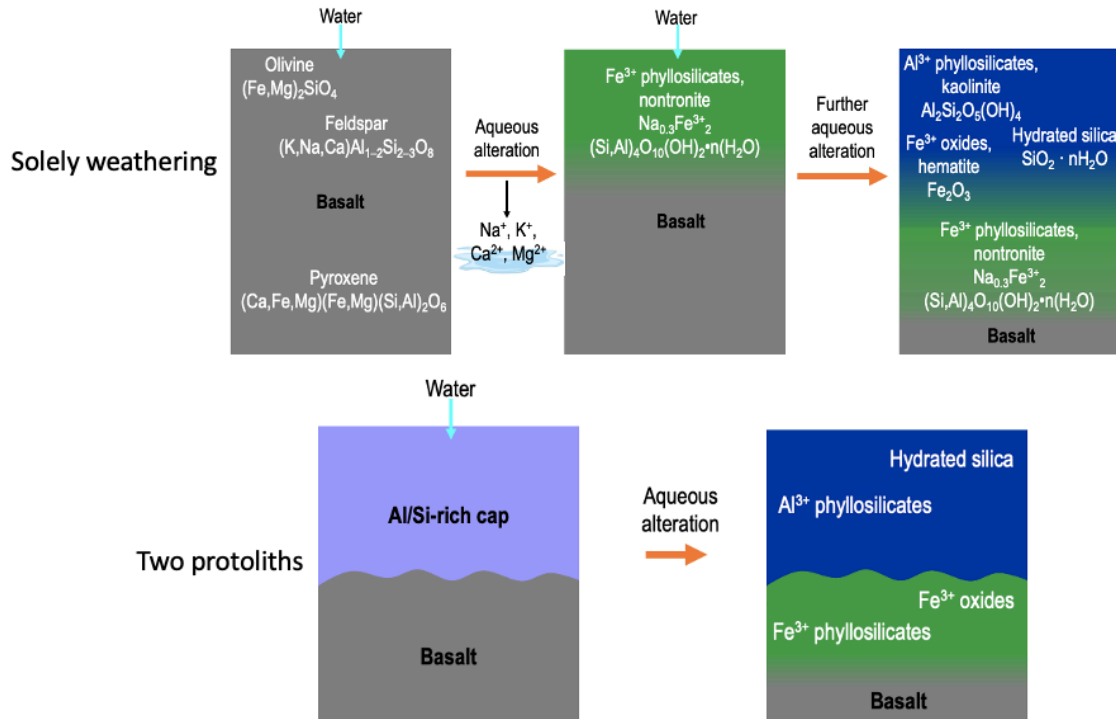


Figure 2: Possible endmember weathering scenarios for the formation of Al-phyllsilicate overlying Fe/Mg-phyllsilicate. a) Alteration of a basalt protolith under oxidizing, neutral-pH conditions. When water is added from the top down, first soluble cations such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} are leached from the system and Fe³⁺ phyllosilicates such as nontronite form. If aqueous alteration continues, then Al-phyllsilicate such as kaolinite forms in addition to hydrated silica and Fe oxides. In this case, there is a conformable transition between Al-phyllsilicate and the underlying Fe/Mg-phyllsilicate. b) A similar assemblage could be produced by the alteration of a protolith of a different, more Al- and Si-rich composition that is unconformably deposited on top of a basaltic protolith. In this case, aqueous alteration would alter the Al/Si-rich unit directly to Al-phyllsilicate and the basalt to Fe/Mg-phyllsilicate. This creates a sharp contact between the phyllosilicates in the final mineral assemblage.

The interpretation of Al-phyllsilicate as representative of intensive leaching has been complicated by re-examination of the mineralogy of several of these Al-phyllsilicate-bearing sites. Interestingly, Fe oxides are not typically detected with the

Al-phyllsilicate deposits. Al-phyllsilicates have been found to lack associated Fe oxide in Valles Marineris (Le Deit et al., 2012) and parts of Mawrth Vallis, though hematite is mixed with Al-phyllsilicate in limited locations in Mawrth Vallis (Wray et al., 2008). Fe oxides mixed with Al-phyllsilicates are a hallmark of pedogenic weathering on Earth in an oxygenated atmosphere (Nesbitt and Young, 1989; Gaudin et al., 2005; Greenberger et al., 2012). Their absence could indicate formation under more reducing conditions, as reduced Fe^{2+} is more mobile. Additionally, acidic conditions can mobilize even oxidized Fe^{3+} and inhibit the formation of Fe oxides (Blesa and Maroto, 1986). Alternatively, the lack of Fe oxide associated with Al-phyllsilicate could indicate an initially Fe-poor protolith rather than formation from intensive leaching of a mafic protolith.

In addition, alteration products 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 adjacent to Al-phyllsilicates in some of the Martian strata (note: Na-bearing natrojarosite and natroalunite or H_3O^+ -jarosite is also encompassed in our use of “jarosite” and “alunite”). Jarosite has been detected alongside Al-phyllsilicates in Nili Fossae (Ehlmann and Dundar, 2015), Mawrth Vallis (Farrand et al., 2009; Farrand et al., 2014; Bishop et al., 2020), and Valles Marineris (Roach et al., 2010; Weitz et al., 2011; Thollot et al., 2012), and alunite has been detected in Terra Sirenum (Swayze et al., 2008; Wray et al., 2011; Ehlmann et al., 2016; Leask et al., 2024). In Mawrth Vallis, the detection of the hydrated silica phases allophane and imogolite overlying the Al-phyllsilicate might indicate a volcanic ash protolith (Bishop and Rampe, 2016). Jarosite has been detected both overlying (Farrand et al., 2009; Farrand et al., 2014) and likely mixed with (Bishop et al., 2020) Al-phyllsilicate in this region. These minerals have been hypothesized to have formed through alteration by acidic brines released from ice melting (Michalski et al., 2013; Bishop and Rampe, 2016) or as evaporites in small surface ponds acidified by S from dissolved volcanic gasses or alteration of a pyrite-bearing layer (Farrand et al., 2014; Michalski et al., 2013; Bishop et al., 2020). At Terra Sirenum, finely-laminated Al-phyllsilicate units thinning away from the proposed volcanic source of Arsia Mons suggest an Al- and Si-rich (non-basaltic) volcanic ash protolith, and jarosite and alunite deposits are interpreted to have formed from upwelling of groundwater acidified by contact with subsurface magmatic sources, jarosite around Fe/Mg phyllsilicates and

alunite around Al-phyllsilicates (Leask et al., 2024). In Valles Marineris, some Al-phyllsilicate overlies Fe/Mg-phyllsilicate similar to other regions in what has been interpreted to have formed through extensive top-down pedogenic weathering (Le Deit et al., 2012). A possibly distinct kaolinite unit is observed in parts of Valles Marineris *underlying* Fe/Mg-phyllsilicate, with probable jarosite associated locally with Fe/Mg-phyllsilicate (Roach et al., 2010). The hydrated minerals in these regions were likely formed by interactions with groundwater of changing chemistry, including water acidified by magmatic S sources (Roach et al., 2010; Weitz et al., 2011; Thollot et al., 2012).

On Earth, jarosite and alunite form in acidic and oxidizing weathering or hydrothermal environments, often from the weathering of sulfide-bearing rocks (Stoffregen, 1993, Bladh 1982; Alpers et al., 1992; Mavris et al., 2018). Additionally, these minerals can precipitate directly from hypersaline acidic lakes (Long et al., 1992), or they can form from condensation out of fumarolic gases or reactions between these gases and the surrounding rock (Stoiber and Rose, 1974; Zimbleman et al., 2005). Depending on oxygen fugacity and element availability, alunite forms at $\text{pH} < \sim 6.5$ and jarosite forms at $\text{pH} < \sim 4.5$ (Symonds et al., 1994; Poulet et al., 2009; Ehlmann et al., 2016). Therefore, the detection of these minerals in association with Al-phyllsilicates could suggest the formation of the Al-phyllsilicates by acidic weathering under oxidizing conditions or a later acidic overprinting process.

In this work, we examine the formation of Al-phyllsilicate in the region of Nili Fossae. The Al-phyllsilicate here has been previously interpreted to be part of a pedogenic leaching sequence from a basaltic protolith (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 additional targeted CRISM and HiRISE images acquired over the final decade of operations that allow examination of mineralogy with stratigraphy. We therefore re-examine the Al-phyllsilicate-bearing units with all available high-resolution imagery. We begin by developing an automated pipeline to detect and map Al-phyllsilicate and all accompanying minerals that could provide clues to formation conditions across Nili Fossae. This pipeline uses the depth and width of Gaussian curves fitted to electronic and vibrational absorption features to detect and map

Al-phylosilicate, Fe/Mg-phylosilicate, hydrated silica, jarosite, alunite, and Fe oxides. We then combine these mineral maps with high-resolution imagery and digital elevation models to understand the stratigraphy and textures of these mineral deposits and construct a geologic history for the formation of the Al-phylosilicate in the region. Finally, we discuss the implications of this proposed formation history for the chemistry and environment of the region and observations and samples taken by the Perseverance rover.

2 Study Area

Nili Fossae is a region of Noachian geologic units to the northwest of the Isidis impact basin. The fossae are a series of parallel grabens that formed as concentric rifts from deformation following the Isidis impact (Wichman and Schultz, 1989). Using crater counting, the Isidis impact has been dated to approximately 3.9 Ga (Werner, 2005). The dichotomy boundary between the northern lowlands and southern highlands lies to the north of Nili Fossae, where there has been significant erosion of the edge of this unit (Tanaka et al., 2003). It is bounded to the south by the Syrtis Major Planum, a Hesperian-age volcanic unit. Lava flows from this volcano embay part of the western edge of Isidis and fill some of the graben of Nili Fossae (Tornabene et al., 2008). The Nili Fossae region contains evidence of substantial surface/near-surface water flow including fluvial channels, fans, and sapping canyons indicating possibly thousands of years of sustained water flow (Fassett and Head, 2005; Mangold et al., 2007).

Nili Fossae has many units enriched in hydrated minerals, suggesting an extensive history of aqueous alteration. Minerals include phyllosilicates, hydrated silica, zeolites and carbonates (Poulet et al., 2005; Mustard et al., 2008; Ehlmann et al., 2009). Low-calcium pyroxene is abundant in the unaltered terrain in this region, which is distinct from the high-calcium pyroxene-enriched rock of Syrtis Major (Mustard et al., 2005). This region also contains the largest exposed olivine unit on the planet (Hoefen et al., 2003) and was deposited after the formation of the Isidis basin (Mustard et al., 2007; Mandon et al., 2020). The timing of the aqueous alteration relative to the opening of the fossae and the formation of other structural elements in Nili Fossae is unclear, but observations suggest that alteration began before the Isidis impact and continued after it

throughout the Noachian and into the early Hesperian (Mustard et al., 2009; Ehlmann et al., 2009).

In this study, we examine Nili Fossae and all of the area bounded by Isidis basin to the east, Antoniadi Crater to the west, the dichotomy boundary to the north, and Syrtis Major to the south. This region includes Jezero Crater, which is being explored by the Perseverance Rover.

3 Methods

3.1 Data Processing

We examined all map projected targeted reduced data record (MTRDR) CRISM images in Nili Fossae, which totaled 187 MTRDR images. These images were atmospherically corrected, denoised, and map projected as described by Murchie et al. (2007) and Seelos et al. (2024). To further reduce detector noise and column-specific artifacts, we ratioed every spectrum to bland spectra in its image column using a method based on that described by Pan et al. (2017). For each pixel, we used the MTRDR IN file VNIR Sample band to identify its original column in the non-map projected image. We also used the information in this band to identify all other MTRDR pixels that were originally in this non-map projected column. Column-wise spectral ratioing for each pixel was performed using all pixels in these original, non-map projected columns.

As in Pan et al. (2017), the bland spectra in each column were defined as those that had values below the mean + 1.5 * the standard deviation value for several key spectral parameters produced by Viviano et al. (2014). These parameters were: BD530_2, BD860_2, BD1400, OLINDEX3, LCPINDEX2, HCPINDEX2, BD1750_2, BD1900_2, BD2190, BD2250, BD2265, BD2290, and BD2355. In addition, we calculated the integrated area between the spectrum and a convex-hull continuum fit in the wavelength range from 1869 to 2417 nm, where most of the diagnostic absorptions of interest for this study occur. Of the spectra in each column that met the first threshold to be considered bland, we chose those with the 9 smallest areas in this wavelength region, and the mean of those spectra became the denominator for the spectral ratioing for that column. As in

Pan et al. (2017), if no spectra in a column met the first threshold, the mean of all spectra in that column was taken as the denominator for ratioing. A Savitzky-Golay filter was then applied to each ratioed spectrum to provide further denoising; we chose a bin width of five channels and a polynomial order of two, parameters that were found not to shift the wavelengths of absorption features.

A challenge in automated processing was that some images actually lack qualitatively bland spectra, even though they do have spectra that meet the quantitative criteria. That is, some spectra identified as bland denominators by the first step still have visible mineral absorptions in this wavelength range. In particular, for several images with substantial areal coverage of Fe/Mg-phylllosilicate, this algorithm selected Fe/Mg-phylllosilicate-bearing spectra as “bland” because their band depths were below the mean + 1.5 * standard deviation threshold. This issue generated a large number of false positive detections of Al-phylllosilicate in those images. We therefore established a flag for these problematic images. Images were flagged as having this issue if the value of the mean + 1 standard deviation of the Fe/Mg-phylllosilicate band depth parameter (BD2290, Viviano et al., 2014) for all the designated bland spectra in the image was greater than 0.0045. For these images, the mineral identification algorithms were applied as described below, but they were examined after to manually refine maps of Al-phylllosilicates generated initially using the section 3.2 approach.

3.2 Mineral Identification

To map alteration phases in CRISM data, we examined the depth of the phases’ diagnostic absorptions in the spectra in the range 1000–2600 nm from the “L” data cubes and the 437–1000 nm range from the “S” data cubes (Table 1). Al-phylllosilicates, Fe/Mg-phylllosilicates, jarosite, alunite, and hydrated silica all possess diagnostic absorptions around 2100–2300 nm, requiring careful analysis of absorption center wavelength and shape to distinguish them (Figure 3). We also found that traditional methods of visually examining maps of band depth calculated as the difference between the reflectance of a spectrum at a given wavelength and the reflectance at that wavelength along a straight continuum (e.g. Viviano et al., 2014) were insufficient for consistently

identifying these minerals, especially jarosite, which we found often has a subtle absorption, particularly when mixed with Al-phyllsilicate. We therefore developed and implemented a method of using Gaussian fitting to the diagnostic absorptions to map the depth and position of the key absorption features and also to automatically identify the presence or absence of each mineral in every pixel for large numbers of images.

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	$(\text{Na},\text{Ca})_{0.3}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2215	Al-OH vibrational
Fe/Mg-phyllsilicate	Nontronite	$\text{Na}_{0.3}\text{Fe}_2((\text{Si},\text{Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2285	Fe-OH vibrational
	Saponite	$\text{Ca}_{0.25}(\text{Mg},\text{Fe})_3((\text{Si},\text{Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$	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.

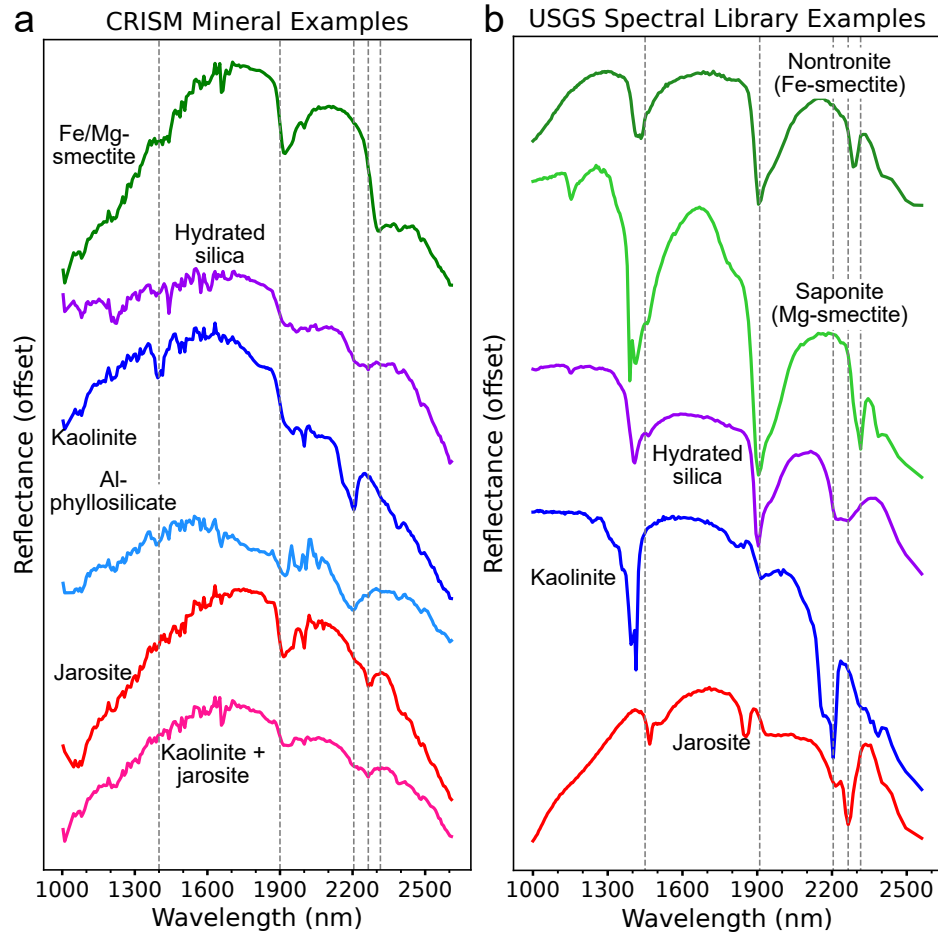


Figure 3: a) Representative examples of spectra from Nili Fossae CRISM MTRDR I/F images that contain alteration minerals. Each spectrum is the average of ~100 pixels from FRT0000A053 (Fe/Mg-smectite, kaolinite + jarosite), FRT000051EE (hydrated silica), FRT0000C202 (kaolinite), FRT00009971 (Al-phyllsilicate), and HRL0000AB0A (jarosite). b) Representative examples of spectra taken in the laboratory from the USGS spectral library (Kokaly et al., 2017)

Gaussian curves were fit to the ratioed and smoothed spectra using Python's `scipy.optimize curve-fit` algorithm, which uses non-linear least squares fitting. Because absorption positions are directly proportional to energy, we first converted the data from wavelength to wavenumber and then continuum-removed each spectrum with a straight line fit across the wavelength range listed in Table 2. For each image, three iterations of Gaussian fitting were applied: one round to detect minerals with absorptions near 2200

nm including Al-phyllsilicate, hydrated silica, and alunite; an iteration to identify Fe/Mg-phyllsilicate; and an iteration to identify jarosite. In each case, Gaussian curves were only fit to pixels that met certain band depth criteria (Table 2) to exclude the processing time of fitting curves to spectra that did not obviously contain the target mineral.

A single Gaussian curve was fit to the spectra to identify Al-phyllsilicate, hydrated silica, alunite, and Fe/Mg-phyllsilicate, but two Gaussian curves were fit to the spectra to identify jarosite. In Nili Fossae, jarosite is commonly found spectrally mixed with kaolinite (e.g. Figure 3). We therefore chose to fit two Gaussian curves to the wavelength range of the kaolinite and jarosite absorptions with the center locations of these curves fixed at the wavelengths of these mineral absorption centers (~2205 and ~2265 nm, respectively). This helps isolate the jarosite absorption without the fitting being as impacted by the presence or absence of kaolinite in the same pixel. For the purposes of identifying the presence and absorption depth of jarosite, only the depth of the Gaussian curve centered at 2265 nm was considered because other diagnostic absorptions of jarosite in other wavelength ranges are weaker and were sometimes, but not always, present.

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 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

Jarosite	2	Depth, width	Center wavelength s	2112.87 nm –2331.02 nm	Fixed at 2265.01 nm and 2205.07 nm	BD2265>0.00 3 and R2284.72>R2 264.88
Fe oxide	1	Depth, center wavelength, width	N/A	442 nm – 631 nm	400 nm – 600 nm	BD530 > 0.16, fit Gaussian depth > BD625

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.

For a pixel to be considered to contain the relevant absorption feature for each round of mineral identification, the depth of the fit Gaussian has to exceed three times the mean standard deviation of the noise of the ratioed bland spectra in the same wavelength range to which the Gaussian is fit. Once this thresholding was complete, we applied a filter to remove all detections that were only a single column width to reduce noise from column artifacts. With this process, we generated thresholded maps of the representative absorption depth for the minerals of interest. These detections were corroborated by hand by analyzing dozens of spectra in each image and comparing to the Viviano et al. (2014) spectral parameter maps.

To identify the minerals creating absorptions at around 2200 nanometers, as multiple minerals in this range were targets of the same iteration of Gaussian fitting, we constructed scatter plots of the Gaussian width and the wavelength of the center of the Gaussian fit and compared these plots to these same parameters for laboratory endmembers from the USGS spectral library (Kokaly et al., 2017) and the Brown RELAB library (Milliken, n.d.) (Figure 4). We visually examined where pixels from each image clustered compared to these endmembers. We also created simulated linear mineral mixtures of endmember kaolinite and jarosite as well as endmember kaolinite and opal (hydrated silica) to understand where those mixtures plot with these metrics. There is some overlap between minerals in this parameter space, but we were largely able to separate kaolinite, montmorillonite, alunite, illite, and opal. We used the appearance of a doublet at 2165 and 2205 nm to confidently identify kaolinite separate from other aluminosilicates. For future analysis, the fit of two Gaussians in this wavelength range

will be compared to the fit of one Gaussian to automatically distinguish kaolinite more robustly.

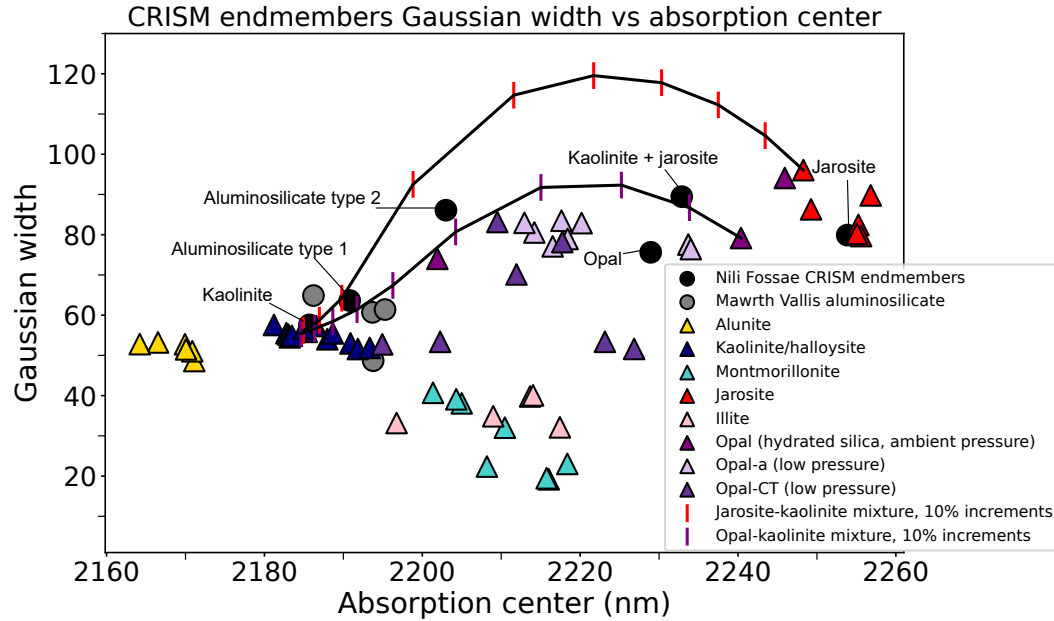


Figure 4: Gaussian-fit width vs. Gaussian-fit center wavelength for minerals with absorptions around 2200 nm and CRISM spectra around Nili Fossae. Also plotted are the same parameters for USGS and RELAB spectral library examples of minerals we considered for identifying the phases present in Nili Fossae as well as spectra of opal-A and opal-CT acquired at Mars-relevant pressure of 0.016 mbar (Sun, 2017) and CRISM spectrum of aluminosilicate in Mawrth Vallis that was identified as allophane/imogolite by Bishop and Rampe (2016).

3.3 Examination of Mineralogic and Stratigraphic Relationships and Context

The thresholded band depth mineral maps were input into ArcGIS Pro for processing. They were georeferenced by hand to the Mars Context Camera (CTX) global mosaic (Dickson et al., 2024) at ~6/m pixel (Malin et al., 2007). Where available, we also georeferenced ~0.25 m/pixel images from the High Resolution Imaging Science Experiment (HiRISE) camera (McEwen et al., 2007). We examined the High-Resolution Stereo Camera (HRSC) 200 m/pixel digital elevation model (DEM) for regional topographic data and to calculate apparent thicknesses of the Al-phylosilicate units. To

understand the stratigraphic relationships, we visually examined all of these different data sets the Al-phyllsilicate-bearing images.

We also examined the geomorphic context of the Al-phyllsilicate deposits at a regional scale using the HRSC DEM. For each deposit, we took note of its location in large (tens of m diameter) impact craters, in large erosional lows, on ridges or mounds, or on intercrater plains. Because the CRISM targeted images examined here do not have global coverage, we compared these observed patterns to the distribution of large Al-phyllsilicate deposits identified in the CRISM multispectral mapping summary products (Pelkey, 2007).

4 Results

4.1 Mineral identification

Using Gaussian fitting, we were successfully able to detect and differentiate alteration phases including Al-phyllsilicate, Fe/Mg-phyllsilicate, hydrated silica, and jarosite in CRISM MTRDR images (Figure 5). Spectra of all relevant endmembers identified in Nili Fossae are shown in Figure 6, and their locations on fit Gaussian absorption width vs. absorption center plots are shown in Figure 4.

Based on a combination of these width vs. absorption center maps and visual examination of the spectra, we determined that all or nearly all Al-phyllsilicate in Nili Fossae is kaolinite or another kaolin-group mineral such as halloysite, like prior studies (e.g., Ehlmann et al., 2009). This identification was based on the clear presence of a doublet at 2165 and 2205 nm (Figure 6), or a close match for the fit Gaussian center and width of laboratory kaolinite where spectra lack a distinctive doublet, likely due to lower crystallinity. The center of the fit Gaussian is around 2190 nm (Figure 4). The kaolinite spectra contain a distinctive absorption at 1900 nm which indicates the presence of H₂O rather than just OH. Because kaolinite has no stoichiometric H₂O, this suggests halloysite or a mixture with a hydrated phase. We determined that there is no unit spectrally dominated by montmorillonite in this region based on the non-occurrence of its narrow, symmetric absorption centered around 2210 nm.

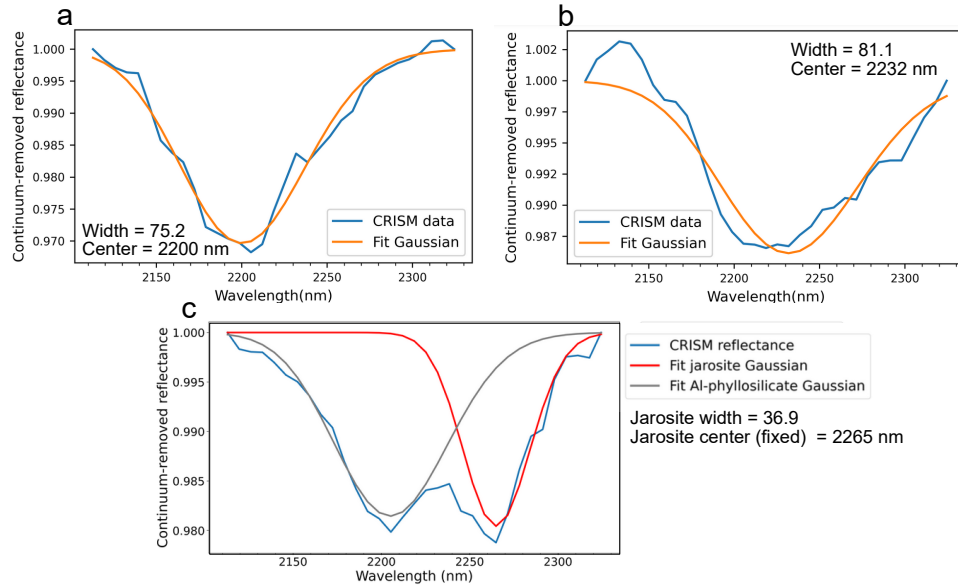


Figure 5: Examples of Gaussian curve fits to continuum-removed ratioed I/F spectra of a) kaolinite (from FRT0000A053), b) opal hydrated silica (from FRT000051EE), and c) kaolinite mixed with jarosite (from FRT0000A053). Note that the Gaussian curves do not perfectly fit the spectra, but the Gaussian depth and width match closely, and the center Gaussian position is representative of the absorption minimum wavelength and shifts systematically with mineralogy (see text).

We identified two hydrated silicate/aluminosilicate phases that lack the distinctive doublet of kaolinite (Figure 6). They may represent mixtures and/or poorly crystalline phases. Aluminosilicate 1 has an absorption minimum of 2186 nm and fit Gaussian center of 2195 nm. In center and width, it appears consistent with aluminosilicate identified in Mawrth Vallis that was classified as possible allophane and/or imogolite (Bishop and Rampe, 2016), or possibly beidellite. Aluminosilicate 2 has a wider absorption with a minimum and fit Gaussian center at 2205 nm and, from the width and center position, could be a mixture of kaolinite with silica and/or jarosite. Finally, we detected hydrated silica across Nili Fossae that is most consistent with opal, consistent with prior studies (e.g., Ehlmann et al., 2009; Smith et al., 2013). This phase was identified through its wide absorption centered between 2220–2250 nm.

CRISM Mineral Examples USGS Spectral Library Examples

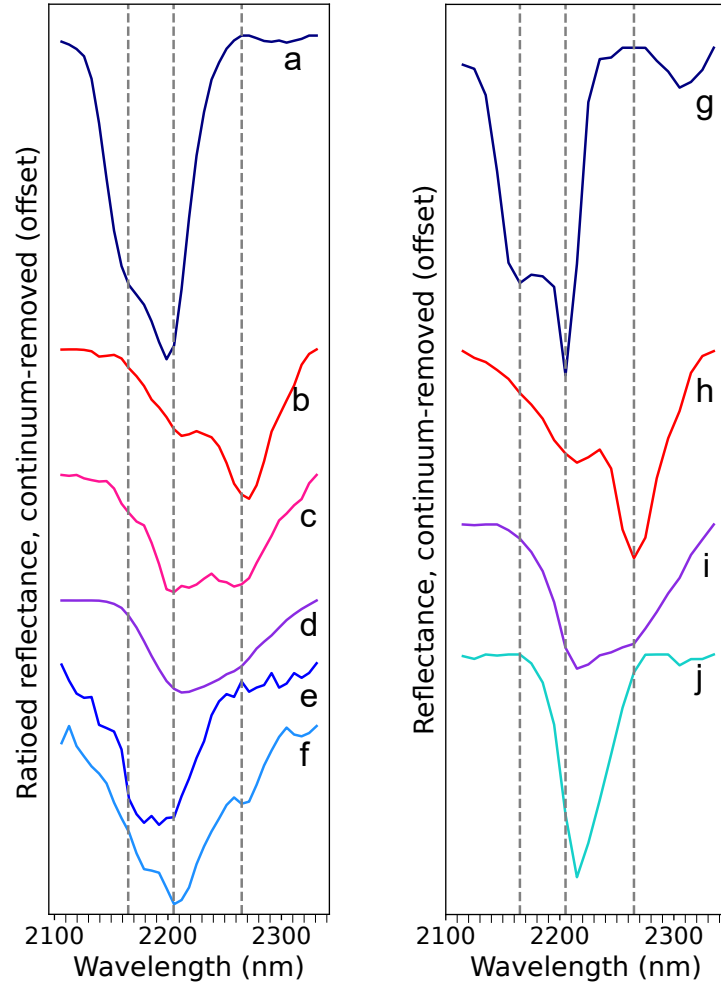


Figure 6: Representative examples of spectra with absorptions around 2200 nm that are observed in Nili Fossae. On the left are continuum-removed ratioed CRISM MTRDR I/F spectra. Each spectrum is the mean of an ROI with 30-1000 pixels. a) kaolinite (from C202, centered on point 155, 577), b) jarosite (from ABOA, centered on point 239, 369), c) kaolinite + jarosite (from A053, centered on point 592, 493), d) opal (from 51EE, centered on point 698, 545), e) hydrated aluminosilicate type 1 (from D6D6, centered on point 254, 593), f) hydrated aluminosilicate type 2 (from 21C5A, centered on point 403, 142). These endmembers correspond to those plotted in Figure 4. On the right are continuum-removed spectra taken in the laboratory from the USGS spectral library (Kokaly et al., 2017) for reference. g) kaolinite, h) jarosite, i) opal, j) montmorillonite.

We identified jarosite based on the Fe-OH absorption at 2265 nm. We also identified dozens of pixels in several images with absorptions at both 2205 and 2265 nm of varying strengths. We interpret this as a pixel-level mixture of kaolinite and jarosite. The distinctive kaolinite doublet is not visible in the spectra of these mixed pixels.

However, we identify the component of the mixture that absorbs at 2205 nm to be kaolinite because of the wavelength of the absorption center and the clear kaolinite absorptions in pixels surrounding these mixed pixels. The double Gaussian curve-fitting algorithm was able to detect jarosite even when only small amounts of it were mixed with kaolinite, enabling the mapping of mixtures.

We detected a phase with two broad absorptions in the short range visible–near-infrared centered at 530 nm and 890–920 nm, respectively. We identify this phase as most likely an Fe oxide and ascribe the 530 nm absorption to Fe charge transfer and the 890–920 nm absorption to an electronic Fe absorption. However, the phase we detected is not a clear match for a single Fe oxide phase. The 530 nm absorption is most similar to crystalline red hematite, but hematite has an electronic absorption at 860 nm, short of the absorption observed here. The 890–920 nm absorption is a better match for lepidrocrocite—metastable $\text{FeO}(\text{OH})$ —or an orthopyroxene such as enstatite (Figure 7), though these pixels do not have the ~1800–2000 nm absorptions characteristic of low-calcium pyroxene. Thus, this phase is 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 scarp edges.

We also searched for and did not find several other alteration products that act as indicators of chemical weathering conditions. Illite has been detected in the Nili Fossae region (Ehlmann et al., 2009), but none was found to be associated with these more aluminous deposits. We found that Nili Fossae lacked minerals with a 2165 nm absorption that would indicate the presence of alunite in this region.

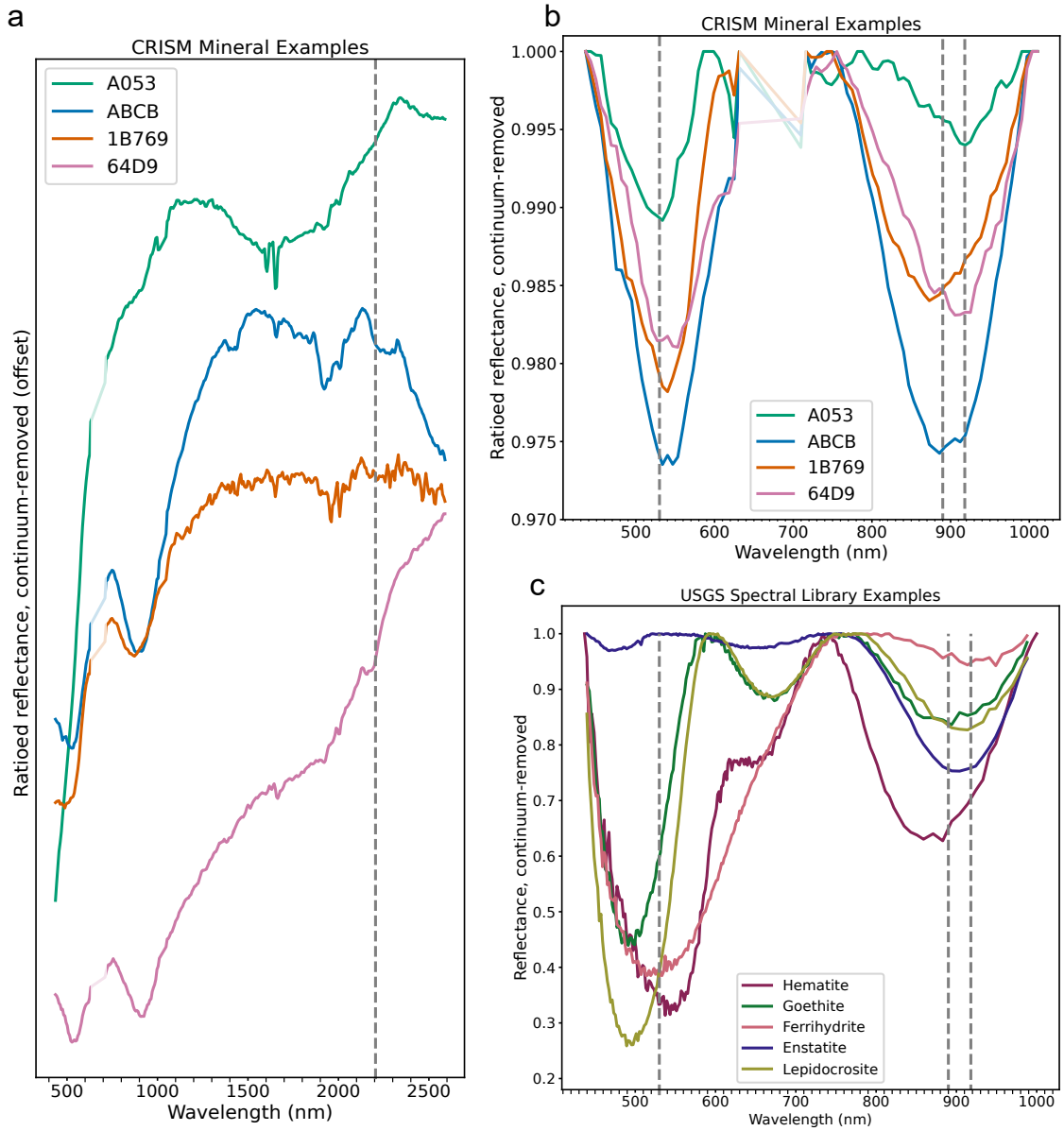


Figure 7: Representative examples of spectra of the minerals absorbing around 500 nm and 900 nm that are observed in Nili Fossae compared to laboratory samples. a) Full wavelength range ratioed CRISM MTRDR I/F spectra. Each spectrum is the mean of an ROI with 100s of pixels from A053, centered on point (530, 540), ABCB, centered on point (368, 470), 1B769, centered on point (196, 196), and 64D9, centered on point (98, 670). b) Short wavelength range continuum-removed spectra of the ROIs plotted in (a). The obscured area between 631 nm – 710 nm represents a CRISM filter break (Murchie et al., 2007). c) Continuum-removed spectra of Fe oxides and pyroxene taken in the laboratory from the USGS spectral library (Kokaly et al., 2017) for reference.

4.2 Regional-scale context of kaolinite

These results show that the alteration products kaolinite, Fe/Mg-phyllsilicate, and hydrated silica are widespread in Nili Fossae. We find 56 CRISM MTRDR images of 167 examined that contain kaolinite; most of these images contain multiple exposures or deposits of this mineral at tens-of-meters to few-km scales. This number also includes several images that provide overlapping coverage of the same deposits. We find 3 images containing hydrated aluminosilicate type 1 and 7 containing hydrated aluminosilicate type 2. We find 27 images that contain hydrated silica, again with multiple exposures or deposits in most images and some images with overlapping coverage (Figure 8).

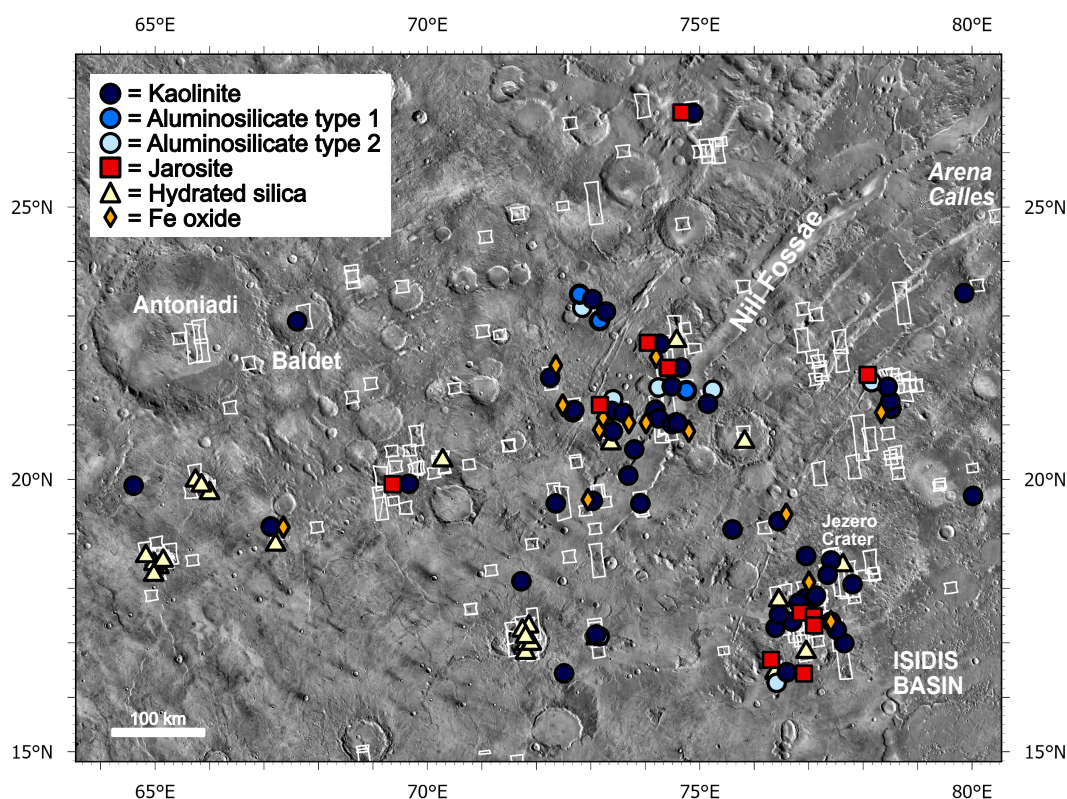


Figure 8: Distribution of detections of the alteration products kaolinite, hydrated aluminosilicate type 1 and 2 (as shown in Figure 6), jarosite, hydrated silica, and Fe oxide in Nili Fossae within CRISM MTRDR images (footprints in white). Basemap is THEMIS daytime infrared.

In agreement with prior findings (Ehlmann et al., 2009, Carter et al., 2015), kaolinite consistently occurs stratigraphically above adjacent Fe/Mg-phyllsilicate. Also as expected (Ehlmann et al., 2009), there are two distinct regions of alteration

mineralogy: kaolinite-rich terrain with accompanying Fe/Mg-phyllosilicate primarily occurs close to the fossae themselves and the edge of the Isidis impact basin, while opal primarily occurs to the southwest on the plains between Syrtis Major and Baldet Crater and is found alongside Fe/Mg-phyllosilicate, illite and chlorite. We did not detect any definitive mixing of kaolinite and opal, nor were they frequently found to occur nearby to each other.

Of the 56 deposits of kaolinite, five also contain jarosite within what appear to be those same stratigraphic units. They are spread out across the kaolinite-bearing regions of Nili Fossae in the images FRT0000A053, FRT00009971, HRL0000AB0A, FRT0000C202, and FRT0000953D. Jarosite is found alongside hydrated aluminosilicate type 2 in FRT00003584. Jarosite was also detected on the margin of the Isidis basin, but these deposits are part of the NE Syrtis layered sulfates as described by Quinn and Ehlmann (2019), rather than in association with kaolinite.

Fe oxide was detected in 13 of the images that contain kaolinite. However, it is not observed to be mixed with detectable quantities of kaolinite in any case, with one possible exception discussed below in section 4.3.1. Instead, Fe oxide appears to occur consistently stratigraphically below the kaolinite. In some cases, it is mixed with Fe/Mg-phyllosilicate, and in others it is not mixed with any detectable mineral phases (though Fe oxide tends to dominate the spectral signature of intimate mixtures, making it difficult to detect any phases with which it is mixed even if they ordinarily have spectral signatures in the VNIR range (Poulet and Erard, 2004; Pan et al., 2021)). We also observe Fe oxide mixed with opal near kaolinite and Fe/Mg-phyllosilicate in FRT0000ABCB and with aluminosilicate type 1 in FRT0000C202.

The geographic and topographic context of the local examples examined in this study are shown in Figure 9.

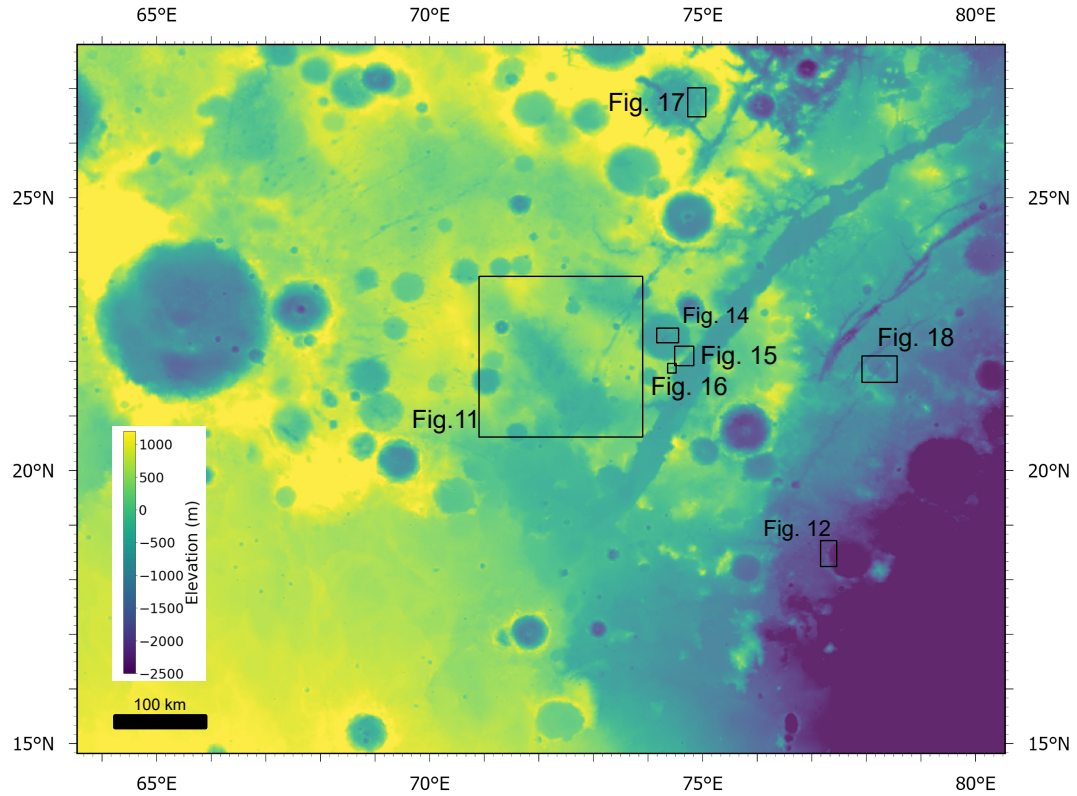


Figure 9: Locations of subsequent figures demonstrating their topographic context around Nili Fossae. Basemap is the MOLA 463 m DEM (USGS).

4.2.1 Topography and kaolinite

In Nili Fossae, kaolinite is associated with large (10s of km)-scale topographic lows including impact craters, large eroded depressions, and within the fossae (Figure 10). Many of these topographic lows show clear evidence for drainage pathways and sediment accumulation. For example, the craters containing images FRT0000A053 and HRL0000AB0A are much shallower than would be expected given their size (Tornabene et al., 2018), suggesting sediment infill. Much of the kaolinite in Nili Fossae is located in four main erosional lows (>50 km): three are to the west of the fossae and run perpendicular to them, and one is in the olivine-rich terrain to the east (Figure 10).

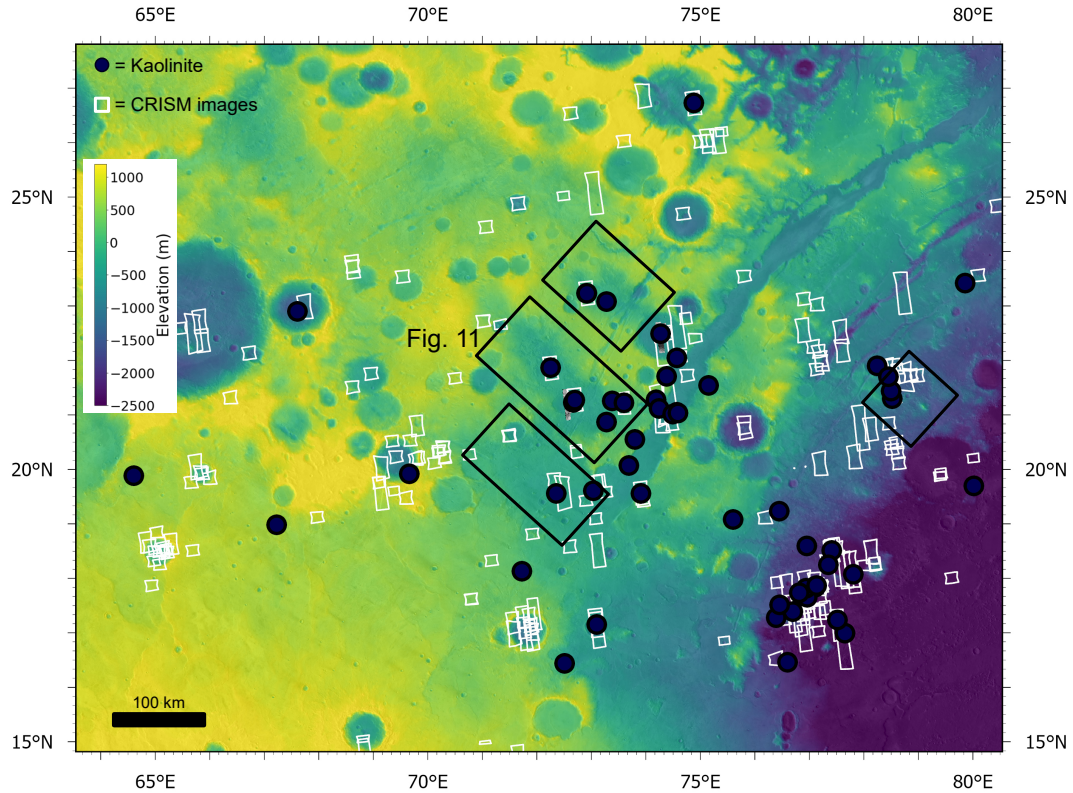


Figure 10: Topographic context of all kaolinite deposits in Nili Fossae. The boxes indicate four large eroded topographic lows that contain kaolinite as described in the text. Basemap is the MOLA 463 m DEM (USGS).

Because the location of the CRISM MTRDR images were targeted to phyllosilicate-bearing areas as identified by the earlier OMEGA mission (Poulet et al., 2005), a robust statistical comparison cannot be done between the distribution of kaolinite in these images and random non-kaolinite points in these images. However, the multispectral CRISM mapping data provides nearly complete, lower-resolution coverage at 180 m/pixel. These data confirm that all large kaolinite deposits visible at this resolution are in impact craters and eroded topographic lows with none occurring on the intercrater plains

4.2.2 Case study of a kaolinite-bearing erosional topographic low (21.3°N, 72.9°E)

As an example, we describe in detail the middle topographic low to the west of the main trough. This depression is approximately 150 km by 50 km, and the six

MTRDR images in this region all contain kaolinite and Fe/Mg-phylllosilicate. The depression has been partially filled with lava flows. Kaolinite and Fe/Mg-phylllosilicate are exposed in the upper portions of the depression that were not embayed by lava or where it was subsequently eroded to reveal the underlying stratigraphic units (Figure 11).

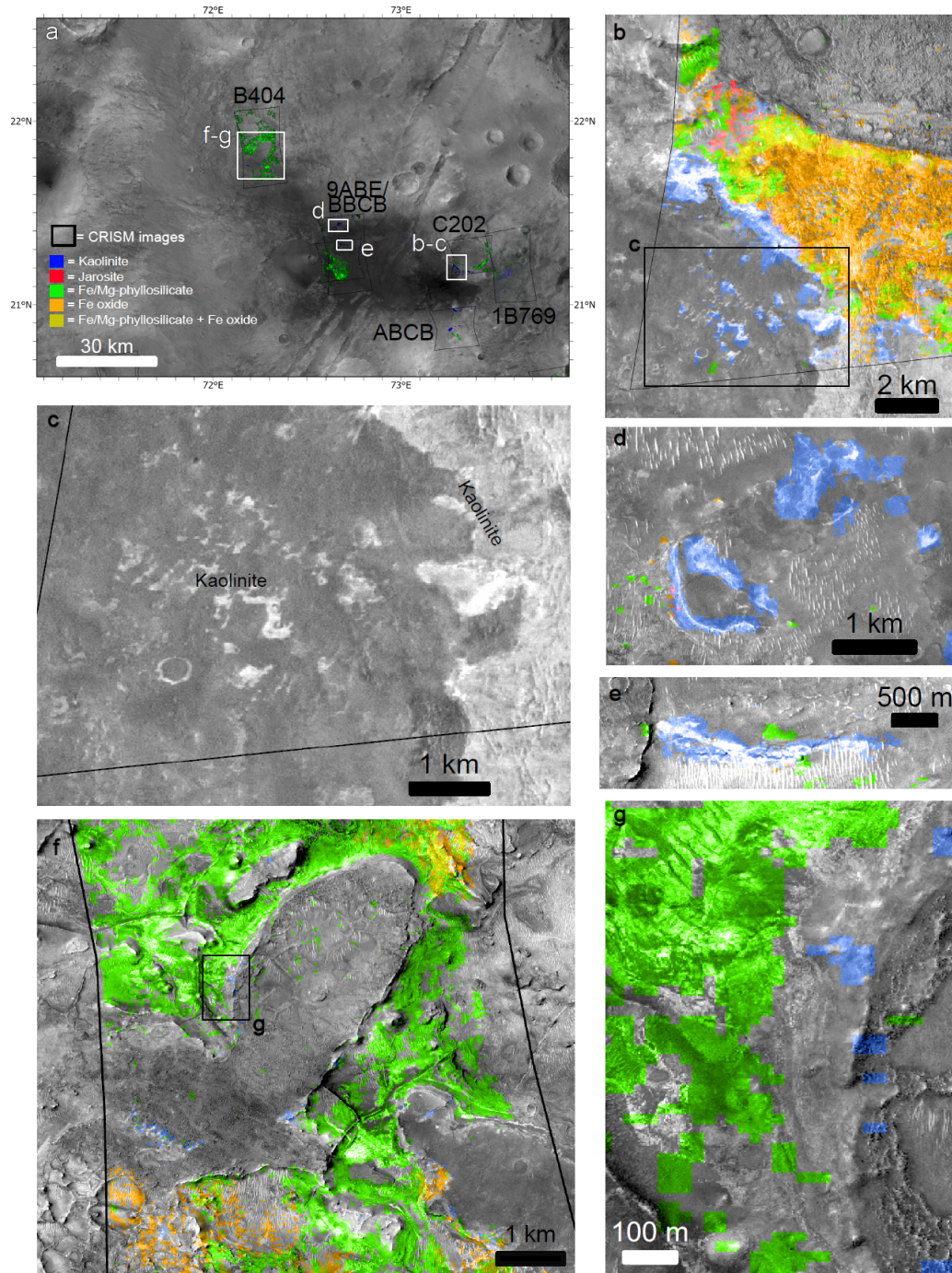


Figure 11: Kaolinite, jarosite, and Fe/Mg-phyllosilicate detections within a large erosional basin to the west of the fossae. a) The erosional basin in CTX. b) An example of the upper portion of the topographic low in image C202 demonstrating the contact between the phyllosilicate-bearing upper unit and the darker lava flows. Kaolinite is exposed on the edge of the upper unit and where it has not been covered by the lava. The adjacent impact crater has excavated underlying Fe/Mg-phyllosilicate, Fe oxide, and jarosite. c) A close-up of the kaolinite in C202 showing the contact between the light-toned kaolinite and the darker-toned lava. d-e) Kaolinite in images 9ABE/BBCB exposed on the edges of scarps eroded through the spectrally-bland lava capping unit. f) Image B404 demonstrating the typical stratigraphic relationship in this region. Kaolinite is exposed on the upper portions of plateaus overlying Fe/Mg-phyllosilicate which is sometimes mixed with Fe oxide. g) Part of a plateau scarp face in B404 showing kaolinite overlying Fe/Mg-phyllosilicate, with the two units separated by spectrally bland material.

Kaolinite is found in two settings in this region. The contact between the lava flows and the older terrain that the lava embayed has kaolinite in the underlying, older material. The edge of the older unit, an erosional remnant as the unit has eroded back, is ringed with patches of high-albedo kaolinite with fine-scale roughness (e.g. FRT0000C202, Figure 11b, c). These kaolinite units are flush with the surface at the HRSC DEM scale (vertical resolution = 10 m (Jaumann et al., 2007)). There are also several kaolinite deposits exposed in scarp faces where there has been erosion through the capping lava unit to the underlying kaolinite-bearing unit (in images HRL00009ABE/FRT0000BBCB, Figure 11d, e) or erosion through a perhaps non-lava spectrally bland capping unit (FRT0000B404, Figure 11f, g). The kaolinite in these scarp faces often has m-scale polygonal fracturing and lacks layering at HiRISE image resolution.

In this basin, kaolinite appears to be stratigraphically above Fe/Mg-phyllosilicate. This is the most evident where kaolinite is exposed in the edges of scarps overlying Fe/Mg-phyllosilicate (Figure 11f, g). In one scarp, there is spectrally-bland material stratigraphically between the kaolinite and the underlying Fe/Mg-phyllosilicate (Figure 11g).

Elsewhere in the unit, impact craters have disrupted the stratigraphy and complicate the interpretation. For example, Fe/Mg-phyllosilicate is seen in overturned material from a small (~10 km-diameter) crater, deposited on top of the kaolinite at the edge of the eroding unit (Figure 11b).

The mineralogy and stratigraphy follow similar patterns in the other parallel eroded topographic lows to the north and south as well as in the olivine-rich terrains to the east of the fossae (Figure 10). In all of these topographic lows, kaolinite is stratigraphically overlying Fe/Mg-phyllosilicate.

4.2.3 Case study near Jezero crater (77.3°E, 18.4°N)

Consistent with previous findings (Tarnas et al., 2019, Scheller and Ehlmann, 2020), we detected a substantial amount of Fe/Mg-phyllosilicate in the Jezero Crater western fan and a small amount of kaolinite in a knob of the inner crater rim unit and in a block on the outside of the rim (Figure 12). Given that it is in the crater rim and does not appear to be in sedimentary fill, it is probable that the kaolinite or its protolith was deposited before the formation of Jezero crater and disrupted. We also corroborated the detection of several small hydrated silica deposits adjacent to the fan (Tarnas et al., 2019), and no kaolinite at orbital scale in the crater-filling deposits.

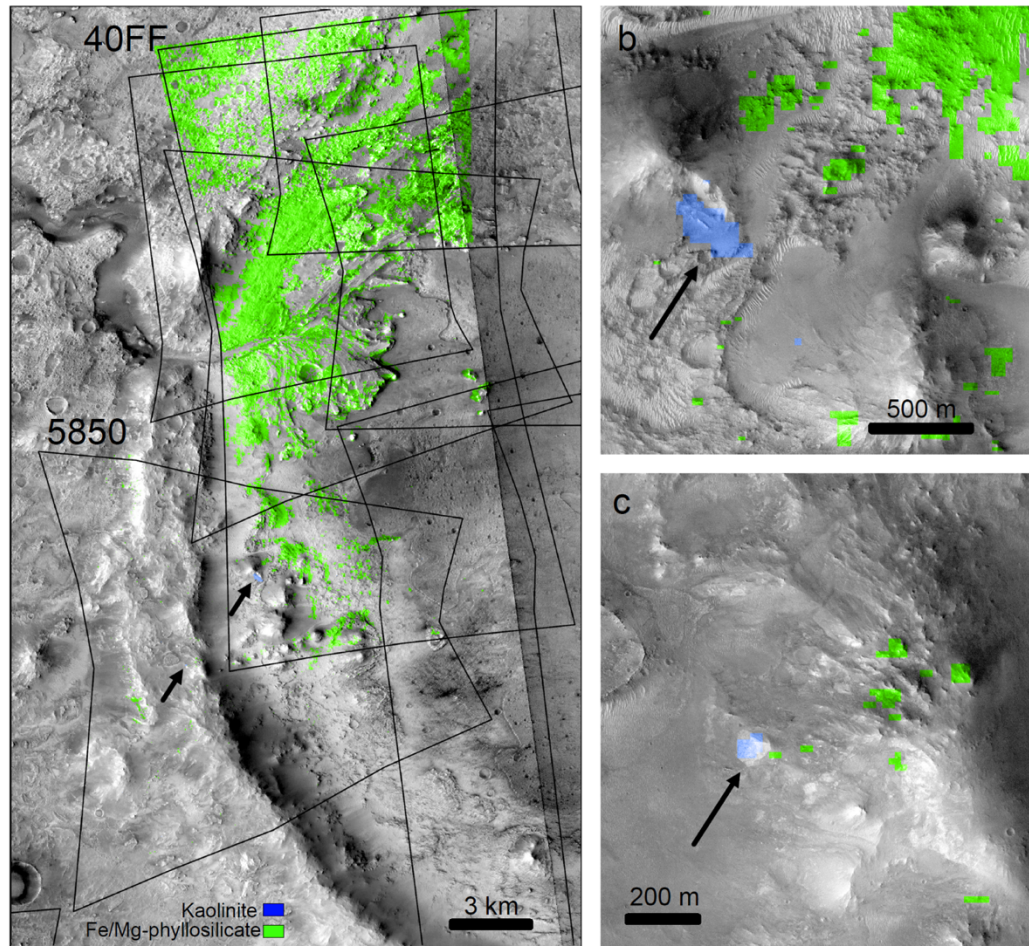


Figure 12: a) Al-phylosilicate and Fe/Mg-phylosilicate mineral map of the western fan of Jezero Crater on CTX imagery. Arrows point to the locations of kaolinite deposits in the crater rim unit, which are shown in more detail in HiRISE imagery in b and c.

4.2.4 Thicknesses of the kaolinite deposits

Where exposures allowed, the apparent thicknesses of the kaolinite deposits were measured with the HRSC DEM (Table 3, Figure 13). Most of the deposits in the present-day exposures are flush with the surrounding terrain and so no thickness could be measured, but several exposures in cliff faces and layered sedimentary deposits allowed for measurement. The apparent thickness of kaolinite deposits in cliff faces ranges from 3–31 m. The thickest deposit of kaolinite in Nili Fossae are layered sedimentary units exposed by a canyon to the northwest of the main trough, where the thickness is at least 135 m. There are no clear spatial trends in the distribution of unit thickness in the region (Figure 13).

Table 3

Kaolinite Unit Thicknesses

Geographic context	Location	Image ID	Stratigraphic context	Apparent thickness (m)
Topographic low to the west of the Nili Fossae main trough	72.3°E, 21.8°N	B404	Eroding out of multi-level cliff faces	3–8 m
Topographic low to the west of the fossae	72.7°E, 21.3°N	BBCB, 9ABE	Eroding out of a cliff face	31 m
Impact crater west of the Nili Fossae main trough	74.3°E, 22.4°N	A053	Eroding out of multi-level cliff faces	14–24 m
Impact crater northwest of the Nili Fossae main trough	74.9°E, 26.7°N	AB0A	Layered sedimentary deposits	18 m, 135 m

Measurements of the thickness of kaolinite units in Nili Fossae where it could be measured from the HRSC DEM.

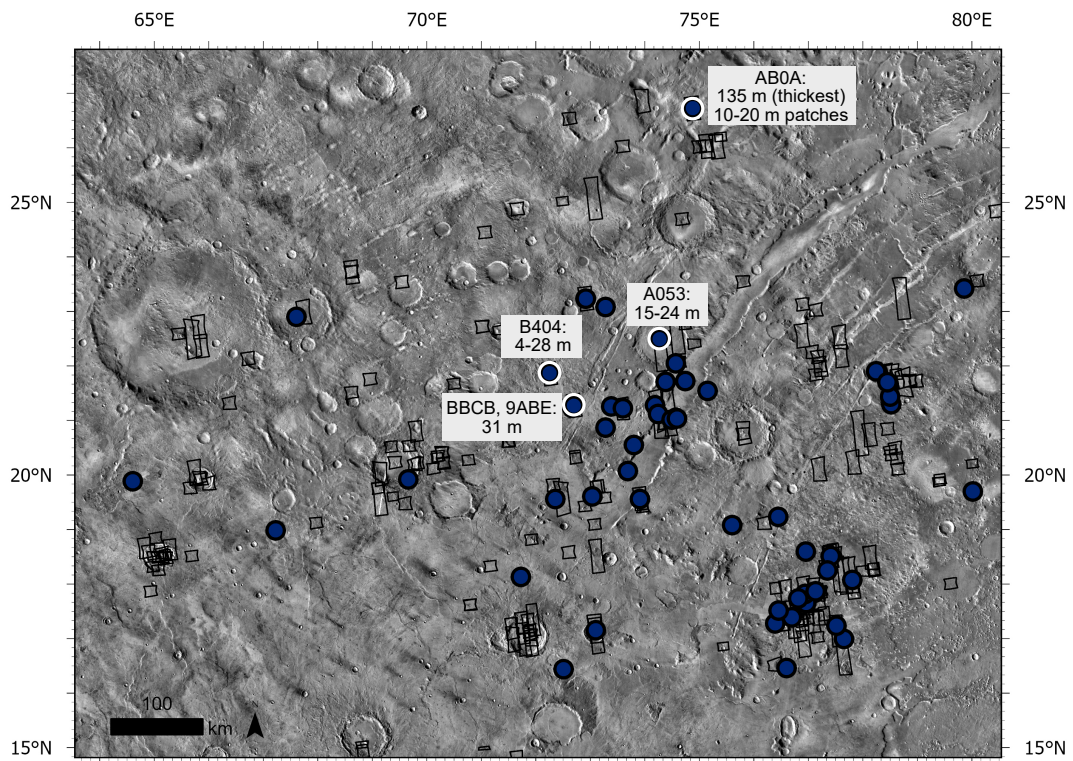


Figure 13: Locations of all Al-phylosilicate detections in Nili Fossae with apparent thicknesses marked for the few images where there was sufficient relief of the Al-phylosilicate deposits for thickness to be measurable in HRSC (BBCB, 9ABE, B404) and CTX (A053, AB0A) DEMs.

4.3. Relationship between kaolinite, jarosite, and Fe oxide

We examine the alteration minerals associated with kaolinite in Nili Fossae. We find that the only other detectable alteration product that is mixed with kaolinite is jarosite. Though Fe oxide is found near kaolinite and sometimes associated with Fe/Mg-phylosilicate, it is never mixed with kaolinite (with a possible exception, see 4.3.1). Here we examine several locations throughout Nili Fossae that cover all jarosite detections and representative examples of the relationships between Fe oxide and other alteration mineralogy.

4.3.1 Nili Fossae main trough (74.3°E, 22.5°N; 74.6°E, 22.1°N)

There are two adjacent kaolinite- and jarosite-bearing images along the main Nili Fossae trough. FRT0000A053 lies within a 45-km diameter, 1-km deep impact crater filled with sediment to the west of the main Nili Fossae trough (Figure 9), previously examined in Ehlmann et al. (2009)'s kaolinite identification. The available CRISM MTRDR image covers the center of the crater, where there is topographic relief from differential erosion and two residual plateaus within a large pit, approximately 11.6 km by 4.6 km and 400 m deep (Figure 14).

Fe/Mg-phylosilicate is the stratigraphically lowest exposed unit in this image; ~300 meters are exposed in the walls of the central pit, and it also is exposed in local lows in the rough terrain to the northeast of the image. Kaolinite overlies the Fe/Mg-phylosilicate in the walls of the pit and on the edges of the residual plateaus (as previously described in Ehlmann et al., 2009). The HiRISE imagery shows that the residual plateaus within the deep central crater pit are formed of several layers (Figure

14b, c). The kaolinite corresponds to high-albedo material exposed around the edges of a layer of these plateaus beneath the bland cap, and this bright material has a m-scale fractured texture that appears to have eroded off of the cliff faces at the edge of the plateaus (Figure 14d). The kaolinite is exposed in the outer rim of the pit as well and likely represents a cohesive layer that formed before the erosion of the pit. Kaolinite is also exposed in small deposits in shallow topographic lows on the plain surrounding the central pit. These topographic lows are eroded into the spectrally bland capping unit (Figure 14g).

There are several jarosite deposits throughout the image. Where jarosite occurs, it is closely associated with kaolinite, usually spectrally mixed at the CRISM resolution of 18 m/pixel. The HiRISE imagery shows that there is no material between the kaolinite and the jarosite; they are in direct contact with each other. In several cases, jarosite appears to correspond to a coherent deposit of lower albedo material that is mixed with the bright kaolinite (Figure 14e). There is also a small deposit of mixed jarosite and kaolinite corresponding to an arc of smooth material in the base of the large eroded pit, 100 m below the other jarosite and kaolinite exposures (Figure 14h).

Fe oxide occurs throughout the image, largely without mixture with other detectable phases, though in some locations it is mixed with Fe/Mg-phylllosilicate. Fe oxide appears to be stratigraphically below the kaolinite and sometimes above Fe/Mg-phylllosilicate where the two are not mixed. This is most apparent within the central multi-layered plateau, where an Fe oxide-bearing layer is exposed between the overlying kaolinite and the underlying Fe/Mg-phylllosilicate (Figure 14b, c, f). The texture of the kaolinite unit (m-scale polygonal fractures) is distinct from that of the Fe oxide layer (smooth) (Figure 14d, f).

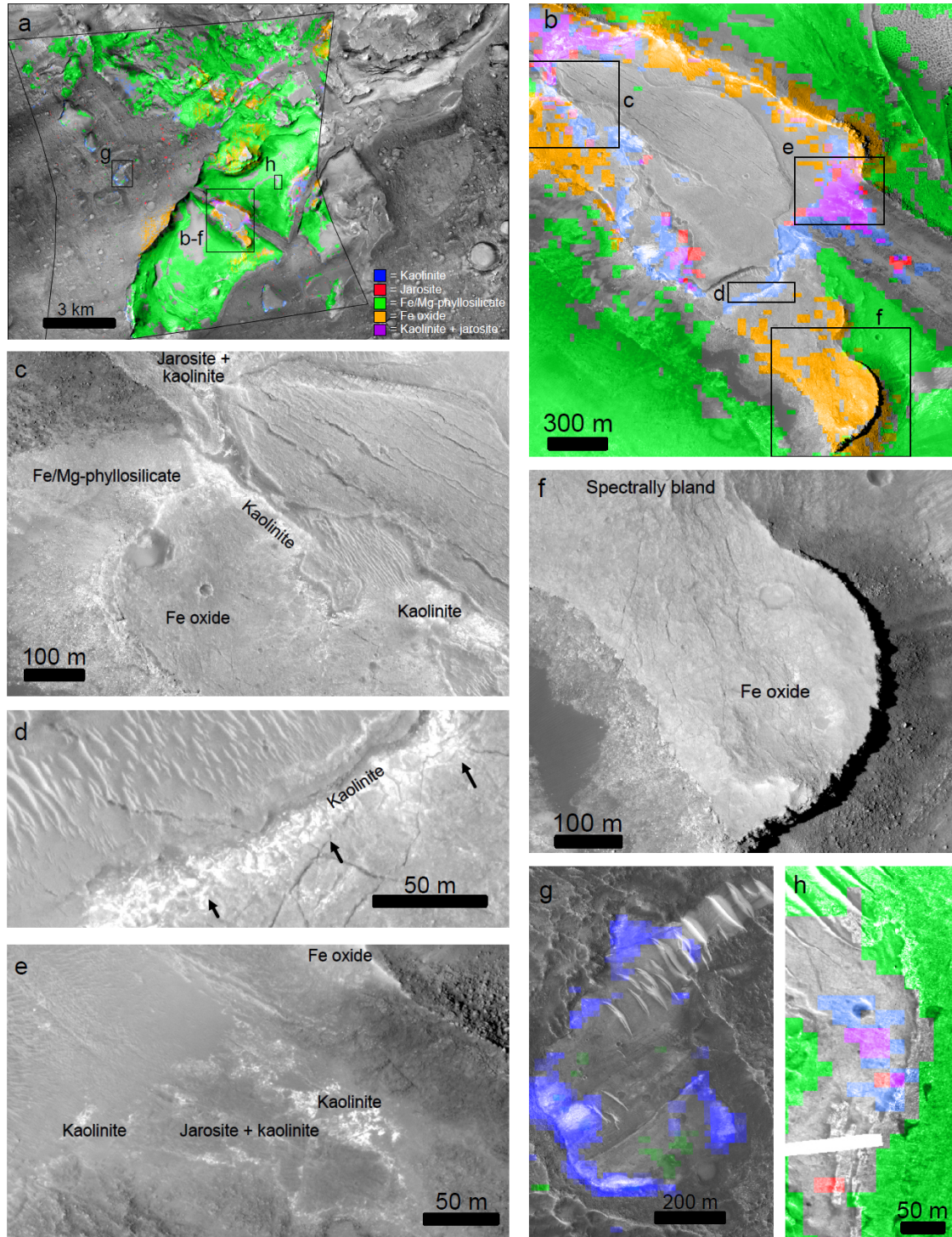


Figure 14: Kaolinite, Fe/Mg-phylosilicate, and jarosite deposits in sedimentary fill in an impact crater next to the main Nili Fossae graben. a) The full mineral map of A053 with a CTX basemap. The large pit carved from aeolian erosion exposes ~300 m of Fe/Mg-phylosilicate, with kaolinite and jarosite around the edges of two remnant plateaus. b) The central remnant plateau demonstrating the stratigraphic layers: a bland capping unit

overlying a kaolinite- and jarosite-bearing unit, overlying an Fe-oxide-bearing unit, overlying Fe/Mg-phyllosilicate. c) A portion of the central plateau in HiRISE image PSP_007345_2025 demonstrating this multi-layered stratigraphy. d) Kaolinite exposed in the edge of the plateau scarp face with a m-scale polygonal fractured texture that is distinct from the underlying spectrally-bland material. e) 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. f) Fe oxide in the central plateau stratigraphically between the kaolinite- and Fe/Mg-phyllosilicate-bearing units. There is no clear tone or texture distinction between the Fe oxide and the spectrally-bland material in this unit. g) Kaolinite exposed in a small topographic low eroded through the bland capping unit. h) A small deposit of mixed jarosite and kaolinite in the base of the eroded pit, deviating from the stratigraphy elsewhere in the image (the white bar is a gap in the HiRISE image).

FRT00009971 is immediately west of the crater containing A053, spanning the top of the crater to the trough floor (Figure 15). Previous analysis (Ehlmann et al., 2009) showed that the portion of the trough wall here has undergone mass wasting, with large slump blocks displaced down the scarp after phyllosilicate formation. Kaolinite is exposed in the promontory between the crater and the trough as well as in the slump blocks on the trough wall and small deposits on the upper rim of the crater. Kaolinite corresponds to high-albedo material in the HiRISE imagery with a similar bright, mottled and/or polygonal texture to that which is in A053 (Figure 15d). Jarosite is spectrally mixed with kaolinite at the CRISM image resolution of 18 m/pixel in the slump blocks. In the HiRISE imagery, this jarosite corresponds to coherent darker patches mixed with the bright kaolinite (Figure 15d, e). The kaolinite on the inside of the crater rim sits both stratigraphically above and below Fe/Mg-phyllosilicate, one of the only places in the region with this ordering (Figure 15b). It may have formed from the impact, perhaps by overturn of the pre-existing stratigraphy or perhaps by impact-induced hydrothermal alteration.

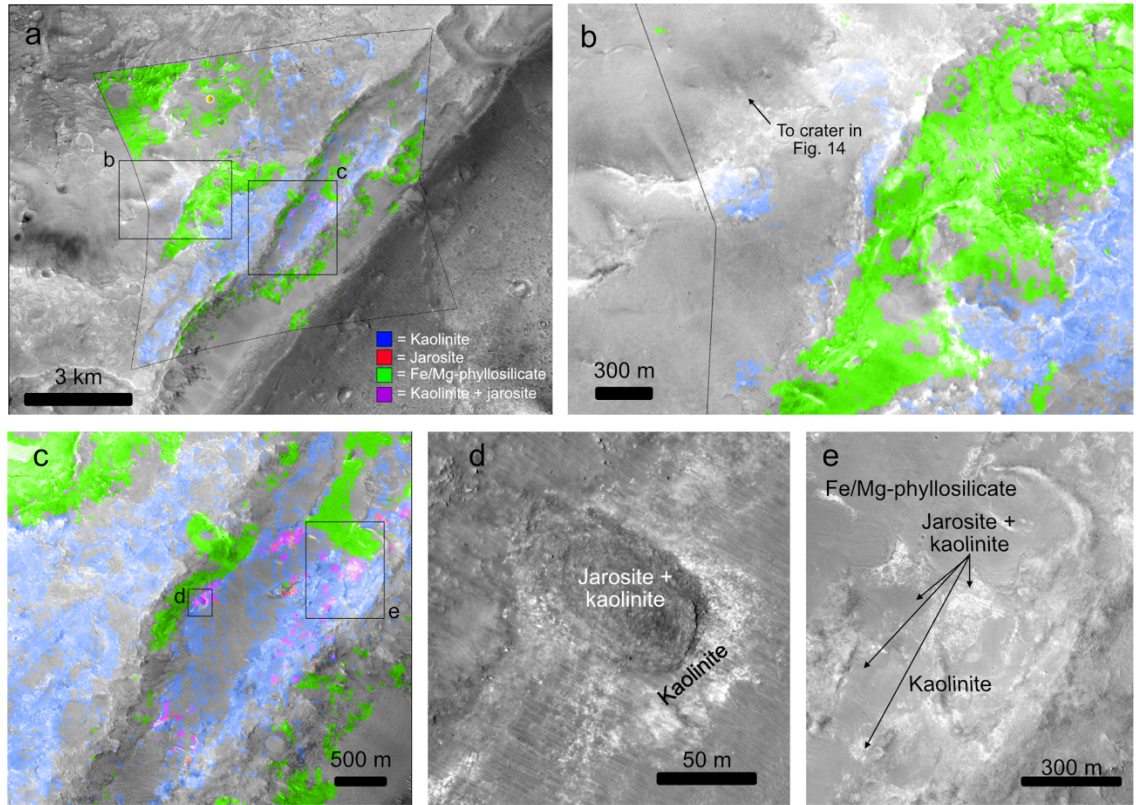


Figure 15: a) The full mineral map of the image FRT00009971 showing kaolinite, Fe/Mg-phyllosilicate, and jarosite on the edge of the main trough and the adjacent crater containing image A053 as shown in Figure 14. b) Some of the kaolinite is exposed along with Fe/Mg-phyllosilicate in the crater wall. c) Kaolinite, Fe/Mg-phyllosilicate, and jarosite exposed on the edge of the trough and in a slump block on the trough wall. d) A coherent dark-toned patch of jarosite mixed with kaolinite and surrounded by lighter-toned kaolinite on the edge of the trough. e) Mixed kaolinite and jarosite as well as kaolinite without a detectable jarosite signature in the trough wall slump block. Their stratigraphic relationship to the adjacent Fe/Mg-phyllosilicate is unclear due to the slumping process.

FRT00009971, along with most images containing kaolinite exposed along the edge of main trough, lacks detectable Fe oxide. One location along the trough edge does contain Fe oxide, image FRT000064D9. Previously studied by Mustard et al. (2009), 64D9 is located south of 9971 along an inlet incised into the western side of the main trough and spans part of the plains above the trough to the trough floor. Fe/Mg-phyllosilicate is exposed throughout the trough wall and in debris along the floor. Kaolinite is exposed on the plain above the trough, largely under the ejecta blanket of an adjacent crater (Figure 16). No jarosite is detected in this area. Fe oxide occurs in three

contexts: on the plains above the trough and the trough floor not evidently mixed with another phase, mixed with Fe/Mg-phylllosilicate on the trough floor (though most Fe/Mg-phylllosilicate in the image lacks associated Fe oxide), and adjacent to and possibly mixed with kaolinite. The mixed CRISM pixels may be an aerial mixture of a brighter, rougher kaolinite unit and a darker-toned, smoother Fe oxide unit rather than intimate mixture, though it is ambiguous with the available image resolution and the stratigraphic disruption caused by an adjacent impact crater (Figure 16b, c). The kaolinite unit on the other side of the inlet in image FRT000078BC has no Fe oxide detected alongside the kaolinite (Figure 16d, e).

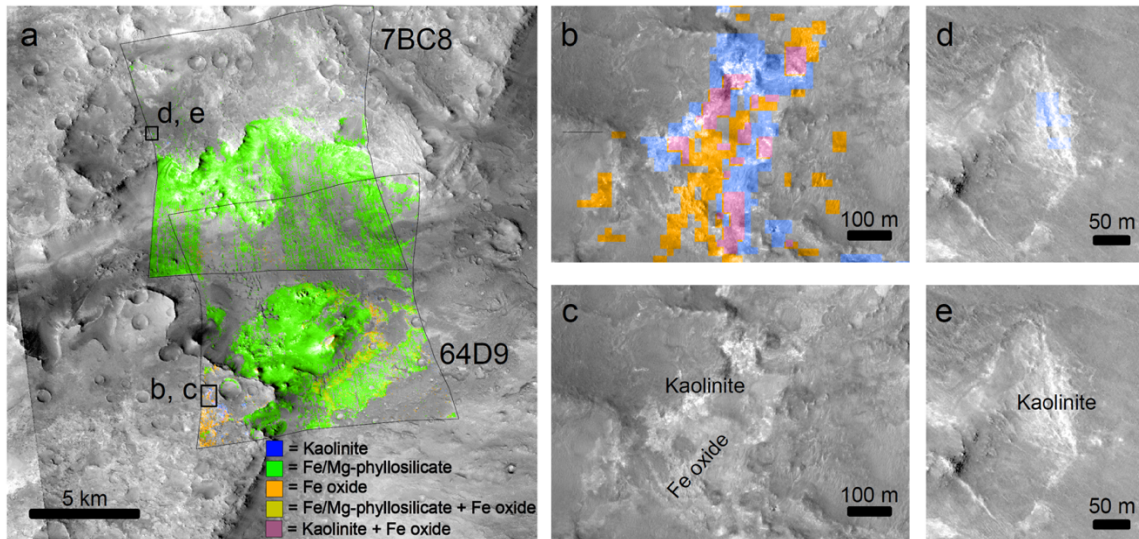


Figure 16: a) The full mineral map of image FRT000064D9 and FRT00007BC8 showing kaolinite, Fe/Mg-phylllosilicate, and Fe oxide along the edge of and within the main trough. b-c) Kaolinite and Fe oxide in 64D9 seemingly partially mixed at CRISM resolution, but the textures of these minerals in HiRISE image PSP_001754_2020 indicate the possible presence of two distinct units. d-e) Kaolinite in 7BC8 across an inlet from the deposit shown in 64D9, likely part of the same unit, that lacks associated Fe oxide.

4.3.2. Northwest of the main Nili Fossae trough (74.9°E, 26.7°N)

HRL0000AB0A is located within a 65-km diameter, 1-km deep impact crater at the northern edge of Nili Fossae to the west of the trough (7). This crater has been heavily modified, including large amounts of sedimentary infill as evidenced by its shallow depth and lack of complex structure given its size (Tornabene et al., 2018). The crater also features polygonal ridge fractures thought to be caused by mineral precipitates in fractures or clastic dikes (Khuller et al., 2021) as well as possible rifts and water-carved inflow channels (Figure 9).

Fe/Mg-phyllosilicate is exposed across most of the crater floor with the remnants of a bland cap unit also visible. Kaolinite, jarosite, and a mix of the two minerals are exposed in numerous deposits, where they mostly occupy present-day topographic lows. No Fe oxide is detected here. The largest jarosite deposit in Nili Fossae is located in this image in a shallow depression approximately 1.5 km by 0.75 km and ~ 5 m deep. This depression is filled with finely-layered (layer thicknesses of <5 – 10 m) kaolinite- and jarosite-bearing sedimentary material (Figure 17b, c). Much of this jarosite is mixed with kaolinite at the CRISM spatial resolution scale of 18 m/pixel with the kaolinite signal strongest around the edges of the depression. The surrounding Fe/Mg-phyllosilicate has a rough, knobby texture and does not exhibit similar layering (Figure 17b, c).

Kaolinite mixed with jarosite is also abundant in the walls of a canyon eroded through fine layers of sediment (Figure 17d, e). Fe/Mg-phyllosilicate in the same rough unit lacking fine layering lies at a higher elevation surrounding the finely-layered kaolinite/jarosite-rich sedimentary material in the depression. The elevation profile across the canyon walls shows that there is no significant slope break and that the kaolinite/jarosite material is unconformably emplaced in the topographic lows (Figure 17e, f).

While current imagery does not include definitive observation of sedimentary layers truncating against the Fe/Mg-phyllosilicate, which would confirm that the kaolinite and jarosite are stratigraphically above the Fe/Mg-phyllosilicate, the distribution of kaolinite and jarosite in cross-section indicates that these minerals likely were deposited on top of Fe/Mg-phyllosilicate in pre-existing topographic lows. An HRSC DEM elevation profile across the image show that kaolinite and jarosite are exposed at many different elevations in the scene relative to Fe/Mg-phyllosilicate (Figure 17f).

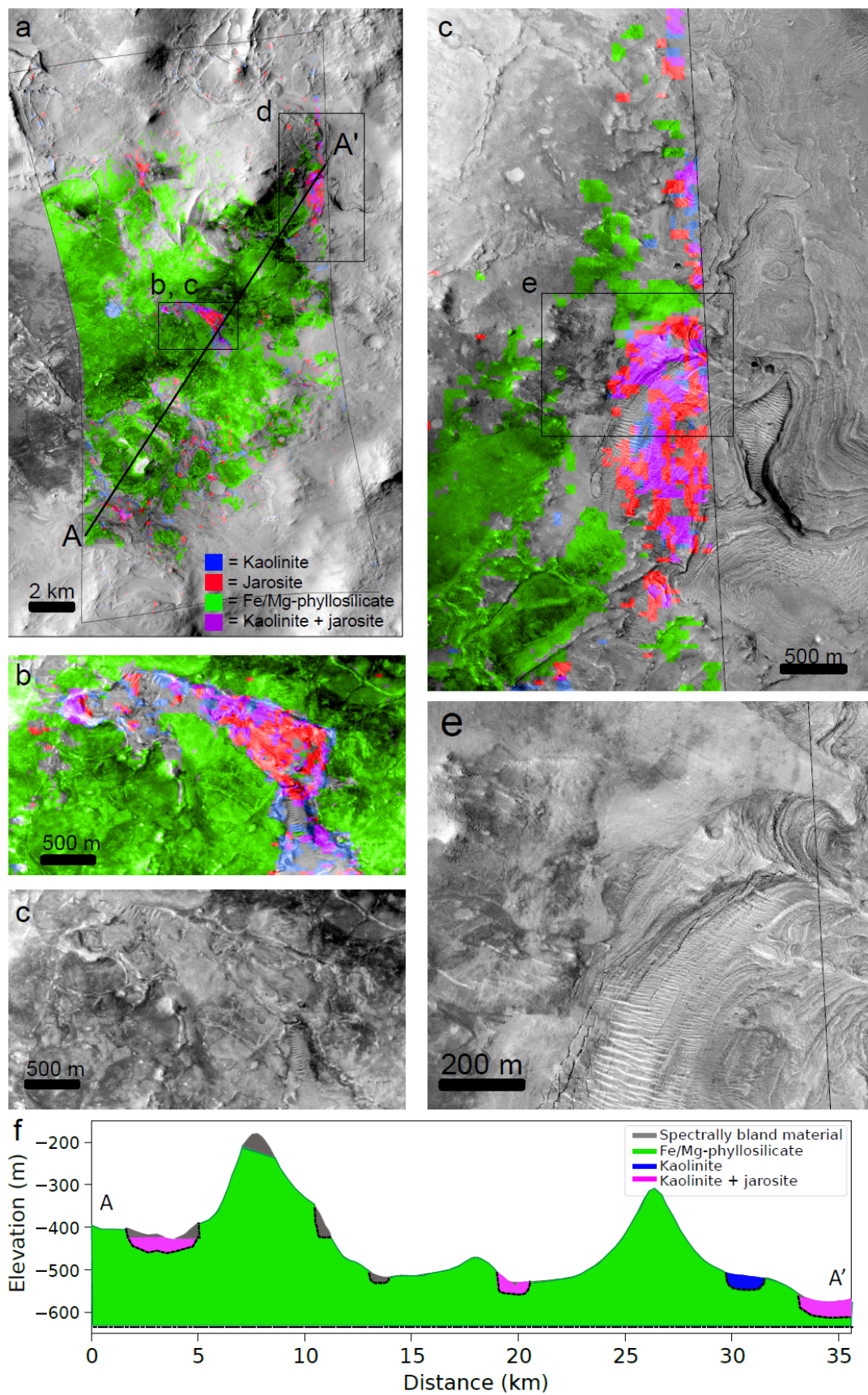


Figure 17: a) The full mineral map of the image AB0A showing Al-phyllosilicate, Fe/Mg-phyllosilicate, and jarosite fill in an impact crater adjacent to the north of the Nili Fossae troughs. The Fe/Mg-phyllosilicate corresponds to a rough, knobby unit that lacks visible layering, while jarosite and kaolinite are mixed in finely-layered sedimentary fill exposed in a shallow pit filled with deposited sedimentary layers shown in the mineral map (d) and CTX imagery (e) and by a canyon carved through this fill shown (d) and at higher-resolution in (e) overlying HiRISE image ESP_086927_2070. f) HRSC stereo DEM transect through the image showing inferred stratigraphy of Fe/Mg-phyllosilicate, Al-phyllosilicate, and jarosite. This transect demonstrates that Al-phyllosilicate and jarosite are exposed primarily in present-day topographic lows topographically below adjacent Fe/Mg-phyllosilicate.

4.3.3 East of Nili Fossae, west of Isidis Planitia (21.9°N, 78.2°E)

An impact crater to the east of the Nili Fossae trough is bisected by a fracture and deformed from its original circular shape to an oblong oval approximately 25 km by 27 km in diameter and 700 m deep (Figure 18). The floor of the crater is primarily olivine and Fe/Mg-phyllosilicate. The fracture through the crater forms a SE-NW valley that is filled with sediment and has some exposed ridges of rock. The ridges are jarosite-bearing, a distinctly different mineralogy than the bulk of the crater floor (Figure 18b). This ridge protrudes through spectrally bland sedimentary fill, and it is composed of rough, high-albedo rock. There is no obvious sedimentary layering, but the visible exposure is limited (Figure 18c).

There is no exposed kaolinite mixed with or adjacent to the jarosite in this location. Instead, there is a small patch of a hydrated aluminosilicate in the rift fill material. This material has a wide, symmetric absorption centered at 2205 nm, consistent with hydrated aluminosilicate type 2 observed elsewhere in Nili Fossae (Figure 6), though the specific composition of this mineral is ambiguous. No Fe oxide was detected in this image.

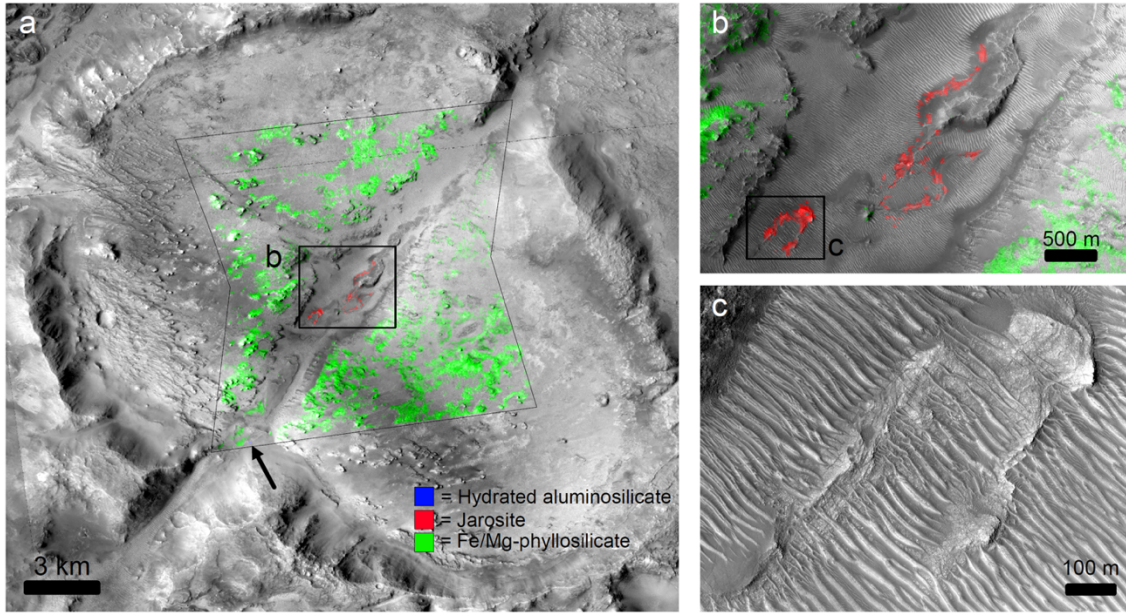


Figure 18: a) The full mineral map of the image FRT00003584 showing Fe/Mg-phylllosilicate on the floor of an impact crater bisected and deformed by a fracture and jarosite in the fill material. The arrow indicates a small amount of hydrated aluminosilicate type 2 in the fill material as well. b) The jarosite-bearing ridge in the center of the fracture, and (c) part of the ridge in higher resolution in HiRISE image PSP_001754_2020.

4.3.4 Erosional topographic low west of the main trough (21.3°N, 72.9°E)

While jarosite is only detected in one location in C202 in this kaolinite-bearing region (section 4.2.2; Figure 11d), Fe oxide is more abundant in this region. All images in this topographic low (C202, 1B679, ABCB, BBCB/9ABE, and B404) contain Fe oxide both mixed with Fe/Mg-phylllosilicate and not evidently mixed with another phase (Figure 11a). In ABCB, some Fe oxide is mixed with hydrated silica adjacent to kaolinite and Fe/Mg-phylllosilicate. The texture of the Fe oxide + hydrated silica unit is smooth, distinct from the texture of the kaolinite (m-scale polygonal fractures) and the Fe/Mg-phylllosilicate (m-scale subparallel roughness) (Figure 19).

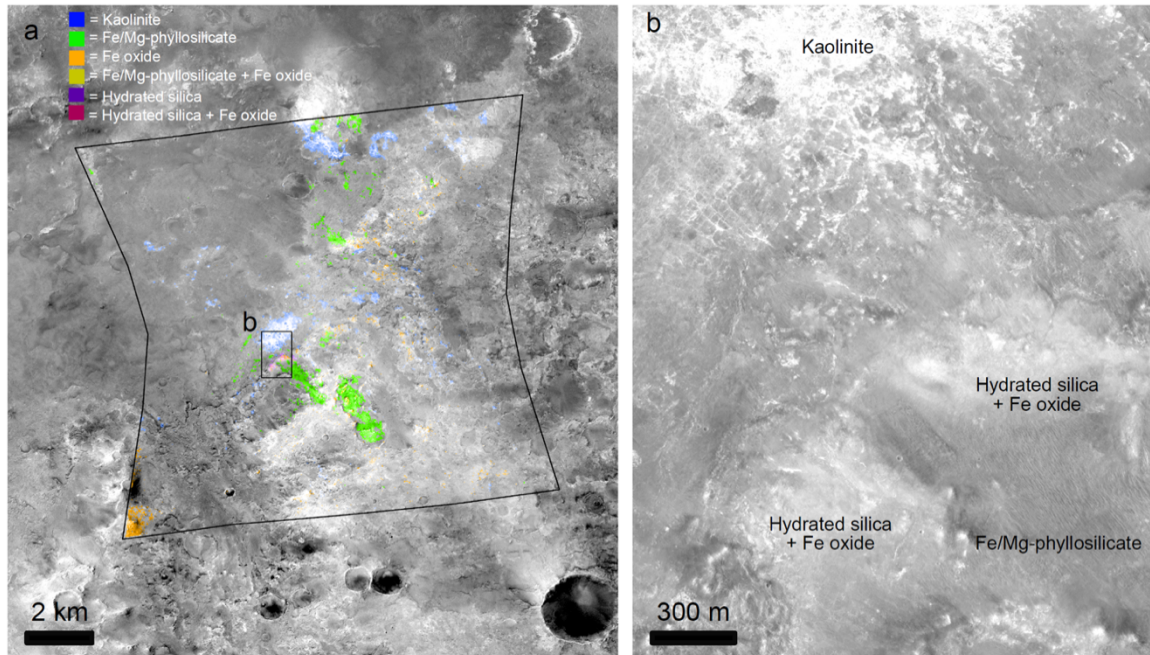


Figure 19: a) The full mineral map of the image FRT0000ABCB showing kaolinite, Fe/Mg-phylllosilicate, Fe oxide, and a small amount of hydrated silica in the large eroded topographic low to the west of the fossae. b) The textures and stratigraphic relationships of these minerals in HiRISE image PSP_001754_2020. Kaolinite demonstrates m-scale polygonal fractures, which is distinct from the smooth hydrated silica + Fe oxide and the Fe/Mg-phylllosilicate.

4.3.5 Disrupted kaolinite and jarosite deposits

Some jarosite deposits nearby kaolinite have been disrupted by impact events and crater slope processes and are therefore no longer in their original stratigraphic context. The kaolinite, jarosite, and Fe/Mg-phylllosilicate deposits in C202 were disrupted by a ~10 km-diameter impact crater in this image (Figure 11d). Additionally, FRT0000953D is located in a 45 km-diameter impact crater in the plains to the west of Nili Fossae between Syrtis Major and Baldet Crater where there are only small, scattered kaolinite deposits exposed (Figure 8). There are small amounts of kaolinite, jarosite, and Fe/Mg-phylllosilicate in the crater wall. The wall has been heavily altered by erosion, slumping, and dry mass wasting processes, so the original stratigraphic contexts of these minerals are indeterminate.

5 Discussion

5.1 Formation of Al Phyllosilicate in Transported Materials

If kaolinite formed with Fe/Mg-phyllosilicate as part of a pedogenic leaching sequence from a basaltic protolith, as has been previously proposed (Ehlmann et al., 2009; Carter et al., 2015), then we would expect to see a conformable, gradational transition between kaolinite and underlying Fe/Mg-phyllosilicate of the same texture in at least some localities. While the transition between Al-phyllosilicate and Fe/Mg-phyllosilicate zones of terrestrial laterites are often considered sharp, there is still several meters of mixing and transition (Gaudin et al., 2005; Gaudin et al., 2011).

Such a progression of mineral assemblage is not consistent with our observations. Throughout Nili Fossae, kaolinite and Fe/Mg-phyllosilicates are almost never spectrally mixed at the scale of a CRISM pixel (18 m) as would be expected for a conformable gradation. The 18 m/pixel scale may be too large to observe the mixed phyllosilicate transition zone seen on Earth. However, in almost all cases, these phyllosilicate minerals appear to correspond coherently to discrete textural units with sharp boundaries in 5 m/pixel CTX or 0.25 m/pixel HiRISE images (e.g. Figure 14c, d; Figure 17c, e). There is sometimes spectrally bland material exposed in between the phyllosilicates, inconsistent with formation as a weathering sequence (Figure 11f). Across Nili Fossae, the textures of the kaolinite and the Fe/Mg-phyllosilicate indicate that they originated from different protoliths and that the kaolinite protolith was transported sedimentary material.

Kaolinite typically appears as high-albedo patches with cm–m scale irregular fractures, possibly indicating desiccation cracks or friable material. The Fe/Mg-phyllosilicate units largely appear knobby, rough, and unlaminated, though some patches have similar fractures to the kaolinite. At some exposures, the kaolinite units exhibit lamination, with layers that contact the Fe/Mg-phyllosilicate unconformably (Figure 17). Kaolinite also can be seen in the exposed edges of several flat, layered plateaus whose structure suggests they may be formed of sedimentary deposits (e.g. Figure 11b, e; Figure 14d, g).

At the regional scale, kaolinite is often associated with sedimentary basins including impact craters and eroded depressions. The kaolinite sediment or its precursor likely accumulated in these topographic lows due to aeolian and/or surface water sedimentary transport processes. We estimate that the abundance of kaolinite in this material is ~5–15% based on comparisons of 2200 nm absorption depth and overall albedo to intimate mixtures of laboratory kaolinite and bland basaltic Nili Fossae CRISM spectra modeled with Hapke modelling.

A possible formation mechanism for the layered kaolinite deposits is that kaolinite formed as part of a weathering sequence, and then erosion removed much of the top section of kaolinite, transporting kaolinite-rich sediment to be deposited in topographic lows. In this case, some of the kaolinite deposits in the region would be from authigenic weathering, and some transported sedimentary deposits. This pre-depositional kaolinite formation scenario is less likely because it is improbable that kaolinite alone would be eroded and transported with no subsequent mixing with the surrounding Fe/Mg-phyllosilicate, and it alone does not explain the observed lack of Fe oxide mixed with kaolinite.

An airfall deposit of ash or pyroclastics produced by local volcanism, followed by syn- or post-depositional kaolinite formation as part of continued regional weathering to form different minerals depending on protolith, is the most straightforward process to produce the observed distinctive high albedo, distinctive texture (sometimes layered), and stratigraphic context of the kaolinite unit regionally. The ash would have been deposited regionally and then reworked through aeolian and/or water-driven erosion and transport. Thin deposits of kaolinite are on the plains, and erosion has exposed tens of meters thick sections in basins (Table 3, Figure 13). This suggests that the basins are accumulating thicker volumes of transported ash than the original airfall deposits.

A volcanic source for the ash is unclear. This is a similar conundrum to the enigmatic origin of the olivine-enriched deposit in the region (Mustard et al., 2009; Mandon et al., 2020; Farley et al. 2022). There are no evident volcanoes in or around Nili Fossae itself, but the large adjacent Syrtis Major volcano is a potential source for the observed amounts of ash (Kerber et al., 2013; Fawdon et al., 2015; Robbins et al., 2011). Fissure volcanism often lacks easily-identifiable features, particularly after several billion

years of continued surface evolution. Volcanic ash deposits are expected to be thickest closest to their source and thin with distance from it. For the kaolinite deposits in Nili Fossae whose thicknesses could be measured, there is no clear pattern in the measured apparent thicknesses that points to the direction of the source (Figure 13), which suggests a complex multi-vent volcanic system and/or points to post-depositional re-working of the ash deposit to accumulate in sedimentary basins.

The mineralogy of the region is consistent with the formation of kaolinite from an Al- and Si-rich (i.e. non-basaltic, non-mafic) ash or volcanoclastic. Given the available resolution of the compositional data and the limits of shortwave infrared spectroscopy, the protolith appears to have weathered into solely Al-bearing phases (apart from jarosite, discussed below), with no Fe/Mg-phylllosilicate or Fe oxides mixed with the kaolinite. The formation of Fe/Mg-phylllosilicate is thermodynamically favored over the formation of Al-phylllosilicate if Fe and Mg are abundant (Chevrier et al., 2007; Velde and Meunier, 2008; Catalano, 2013). Their absence and the alteration of the protolith to primarily Al-phylllosilicate instead suggests an Al/Si-rich, Fe/Mg-poor protolith of a possible felsic to intermediate composition. Fe oxides are normally a residue in terrestrial laterite deposits for weathering under oxic conditions with Fe in the protolith (Nesbitt and Young, 1989; Gaudin et al., 2005; Greenberger et al., 2012). Additionally, this protolith weathered to kaolinite with no to rare montmorillonite or other Al-phylllosilicates that contain the base cations Ca^{2+} , Mg^{2+} , and Na^{+} in addition to Al^{3+} . Formation of kaolinite indicates that weathering occurred with high drainage enabling the flushing of these base cations from the system, or the protolith initially lacked these elements and was predominantly Al, Si-rich (Wilson, 2004). The mineralogy and exposed stratigraphy alone do not differentiate between a meteoric and groundwater source for the alteration.

5.2 Jarosite and Fe oxide as products of localized Fe-bearing water

To form jarosite in a given environment, there must be sufficient Fe and S, pH of 1.5–4.5 (this acidity typically corresponds to the presence of S due to H_2SO_4) (Symonds et al., 1994; Poulet et al., 2009; Ehlmann et al., 2016), and oxidizing conditions. It could be expected, therefore, for acidic alteration to cause jarosite to form in association with

Fe-phylllosilicates, which would provide the requisite Fe. Indeed, it forms in such circumstances in Terra Sirenum (Leask et al., 2024). We would not necessarily expect jarosite to form in association with kaolinite, which contains no Fe.

However, we found the reverse in Nili Fossae: jarosite, where it was detected, is almost always associated with kaolinite, and was never found to be associated with the abundant Fe/Mg-phylllosilicate. Thus, all the conditions for jarosite formation must be present in conjunction with kaolinite, whereas at least one of the conditions for jarosite formation must be absent in conjunction with Fe/Mg-phylllosilicates. We propose that these observations are consistent with a process of jarosite formation from Fe-bearing waters reacting with local in situ S sourced from the kaolinite ash protolith. The Fe oxides identified either in association with Fe/Mg-phylllosilicate or without other detectable phases (but notably, not in association with kaolinite) may have also formed from this Fe-bearing fluid in contact with an oxidizing atmosphere, but where there was insufficient available S to form jarosite.

5.2.1 Jarosite association with phyllosilicates

In Nili Fossae, we do not find jarosite mixed nor associated with Fe/Mg-phylllosilicate. We would expect jarosite to form if the abundant Fe-rich material came into contact with acidic fluids, which would provide the S necessary for jarosite formation. The absence of jarosite in association with Fe/Mg-phylllosilicate suggests that the water was not acidic, and there was a lack of sufficient S locally available from other sources like the Fe/Mg-phylllosilicate protolith.

There is a strong spatial association between kaolinite and jarosite in Nili Fossae that indicates that the conditions necessary to form jarosite were met within the kaolinite-bearing units. Although most of the kaolinite deposits in this region lack nearby jarosite, where jarosite was found, it was almost always adjacent to and/or mixed with kaolinite. This jarosite in this region is found in two contexts: in image AB0A, jarosite is well-mixed with kaolinite in layered sediments (Figure 17). In the other jarosite occurrences, it primarily forms small discrete patches of 0.03–0.15 km² size. The spectra of these patches vary from apparently endmember jarosite to mixtures with varying

quantities of kaolinite. Available HiRISE imagery typically shows that the strongest jarosite signatures correspond to darker terrain that are in contact with higher albedo terrain with a stronger kaolinite spectral signature (Figure 14e, 15d).

The presence of these coherent deposits of jarosite indicates largely authigenic precipitation of jarosite post-sediment deposition as opposed to pre- or syn-depositional formation in which the distribution of jarosite would be dispersed instead. Because jarosite formation appears to be authigenic within the kaolinite, these minerals either formed contemporaneously, or jarosite post-dates kaolinite. In image AB0A, the dispersed jarosite well-mixed with kaolinite could indicate some local post-formation reworking of these units.

5.2.2 Sulfur source for jarosite formation

As discussed above, the absence of jarosite in conjunction with Fe/Mg-phyllosilicate provides evidence that the water available did not contain the S required for jarosite formation. Rather, jarosite's strong association with kaolinite suggests that the requisite S may be provided by the kaolinite protolith itself. This is consistent with the protolith's proposed origin as a volcanic ash, as ashes are rich in S from adsorbed sulfuric gases released by volcanism. On Earth, SO_4 is the most abundant soluble compound in volcanic ash, with a content of 15 parts per thousand, loosely associated with grains rather than bound in glasses (Taylor and Stoiber, 1973). This abundance is likely higher on Mars, where volcanic gases are modeled to contain around 10–100 more S than terrestrial volcanic gases (Gaillard and Scaillet, 2009). If volcanic ash is the source of the kaolinite in Nili Fossae, it could provide the S required for jarosite formation, and so the distribution of jarosite may therefore be controlled by the distribution of local in situ S in this region.

5.2.3 Iron source for jarosite formation

For jarosite to precipitate authigenically within kaolinite using locally-sourced S from the kaolinite protolith, there must also be a source of Fe. Otherwise, alunite would be

expected to form instead (Symonds et al., 1994; Poulet et al., 2009; Ehlmann et al., 2016). Therefore, Fe may be provided by the water that produced the jarosite. We propose that water could become Fe-enriched by dissolving Fe as it percolates through the >100 m of Fe/Mg phyllosilicate underlying the kaolinite.

Once Fe-rich water contacts an oxidizing atmosphere, Fe oxides would be expected to form if little S is present, or jarosite would be expected to form if there is sufficient S present to precipitate sulfates instead. The Fe oxide that occurs throughout Nili Fossae, either mixed with other minerals including Fe/Mg-phyllosilicate (e.g. Figure 11d, 16a) or lacking a detectable mixed phase (e.g. Figure 14), likely also formed from this Fe-enriched fluid. Because much of the Fe/Mg-phyllosilicate lacks mixed Fe oxides, this suggests that the formation of Fe oxides was a local process that may have postdated earlier phyllosilicate formation in less oxidizing conditions. Where this Fe-bearing fluid contacted kaolinite and its local S, all conditions necessary to form jarosite were met, and so jarosite precipitated authigenically in these locations.

The source of the water in this later stage of fluid interaction is indeterminate from our analysis. It may be groundwater or ponding of a later stage of surface water. This is a topic for future study.

5.2.4 Relative timing of phyllosilicate and jarosite formation

After the period of widespread phyllosilicate formation in the Noachian, Mars experienced a shift to widespread sulfate formation (e.g. Gaillard et al., 2013). However, we do not think that the context of the jarosite observed in Nili Fossae is consistent with its formation through these processes. If the jarosite in Nili Fossae formed as part of this widespread period of sulfate formation, then we would not expect it to be preferentially associated with the kaolinite. Rather, we would expect to find jarosite throughout the region associated with Fe-bearing units. That the jarosite is so closely associated with the kaolinite and distinctly lacks an association with the abundant Fe-phyllosilicate in the region indicates that jarosite likely did not form from a sulfur-bearing atmosphere alongside the other widespread sulfates but instead formed from a different process. We

therefore find that a formation process for jarosite in Nili Fossae from Fe-enriched fluid interacting with local sulfur from the kaolinite protolith best matches the observations.

While the alteration mineral assemblages in this region indicate formation of jarosite contemporaneous with or after kaolinite, in the case that jarosite post-dates kaolinite, the possible range of timing between their formations is unclear from the visible mineralogy alone. Because we contend that jarosite did not form as part of the period of widespread Hesperian sulfate formation, any existing gap between their formations need not be representative of the timing of this global transition from largely phyllosilicates to largely jarosite. S adsorbed onto volcanic ash is highly soluble (Taylor and Stoiber, 1973), and so jarosite precipitation would likely occur during the next period of significant water interaction after its deposition.

Jarosite is a metastable phase. With continued contact with water at water/rock ratios of greater than 10, jarosite will eventually dissolve and reprecipitate as iron oxides/hydroxides including goethite ($\text{FeO}(\text{OH})$) and hematite (Fe_2O_3) (Zolotov and Shock, 2005). Therefore, the continued existence of jarosite suggests that it represents the final phase of substantial water interaction with rocks in this region.

There is evidence for liquid surface water activity nearby Nili Fossae that significantly postdates clay formation in the region. In particular, Jezero Crater contains the record of a fluvial system that was likely active several hundred million years after the formation of phyllosilicates in Nili Fossae, though the ages of both are poorly constrained (Loizeau et al., 2012, Carter et al., 2015; Mangold et al., 2020). We propose that jarosite in Nili Fossae most likely formed before the Jezero fluvial system and so survived this aqueous activity. This may suggest that the water that sourced the Jezero system was localized and did not interact with the jarosite in Nili Fossae. Alternatively, the phyllosilicate and jarosite units in Nili Fossae experienced at least one period of subsequent coverage by bland capping unit and later exhumation (e.g. Figure 14). It is possible that if there was later aqueous activity in the Nili Fossae region like precipitation, this water did not contact the jarosite-bearing units because they were buried.

5.3 Proposed Geologic History

Based on the stratigraphy, texture, and geomorphic context of these minerals, we therefore propose the following alteration history of the region. This history is illustrated in Figure 20.

1. The rocks comprising the Nili Fossae region were initially primarily basaltic. Extensive Fe/Mg-phyllosilicate was formed from this basalt either before or during the subsequent formation of kaolinite.
2. Explosive volcanism produced Al- and Si-rich ash in the eastern part of the region. This material was deposited on the plains across Nili Fossae and then locally re-worked by erosion and transported as sedimentary material into topographic lows, both impact craters and large erosional lows acting as sedimentary basins.
3. Within these sedimentary basins, the more Al/Si-enriched sediments were deposited on top of the underlying basalt and/or Fe/Mg-phyllosilicate, via transport processes that generated layering and built up their thickness in topographic lows.
4. Water interacted with the region, and kaolinite was produced from the Al-rich ash. The water could include meteoritic surface water runoff or groundwater. This could be contemporaneous with step 3.
5. Groundwater or another water source enriched with Fe from percolating through Fe/Mg-phyllosilicate upwelled or ponded in some topographic lows. There, it reacted with S from the kaolinite protolith ash to produce authigenic jarosite when in contact with an oxidizing atmosphere. This may be contemporaneous with kaolinite formation and/or anytime thereafter but before the emplacement of the overlying bland unit. Fe oxide precipitated where this water contacted an oxidizing atmosphere but not the S-enriched kaolinite protolith.
6. The phyllosilicate- and jarosite-rich units were covered in a spectrally bland cap unit, likely both basaltic lava flows and sediment deposition.
7. Subsequent aeolian erosion exposed some of the altered terrain. Some of this altered terrain was also reworked by impact events.

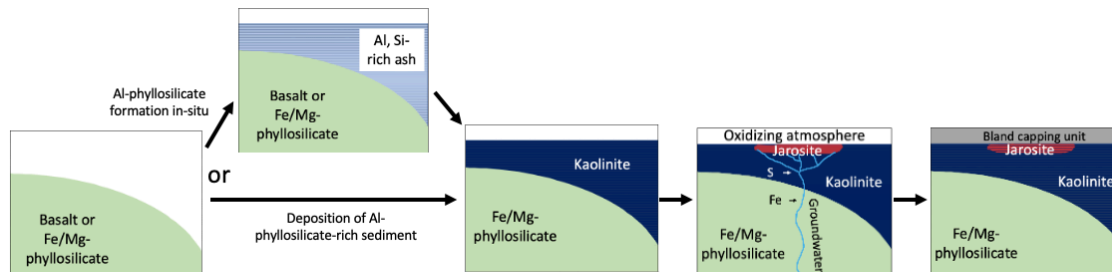


Figure 20: Proposed geologic history for the formation of Al-phyllsilicate in Nili Fossae. We propose that Al/Si-rich ash or Al-phyllsilicate-rich sediment was deposited on top of either basalt or Fe/Mg-phyllsilicate. Phyllsilicate formation occurred either pre-depositionally or in situ from the second protolith. We illustrate our preferred formation mechanism of jarosite, from groundwater enriched in Fe from leaching of Fe/Mg-phyllsilicate and S from the Al-phyllsilicate ash protolith.

5.4 Jezero Crater and the Mars 2020 mission

The presence of the Perseverance Rover in Jezero Crater at the edge of Nili Fossae allows the opportunity to bridge remote sensing data with recent rover observations. Numerous light-toned float rocks have been detected in Jezero Crater, and several that are rich in kaolinite have been analyzed in detail by the Perseverance rover (Royer et al., 2024). These rocks may be related to the kaolinite deposits detected from orbit. These rocks range in apparent texture from sedimentary laminations to pyroclastic/porphyritic. They have abundant Al and low Fe, Mg, and Ca, which could indicate a high chemical alteration index or non-basaltic protolith. The rocks also have anomalously high Ni content in bulk chemical analysis, though it is unclear what its host mineral is. The high Ni content was interpreted by Royer et al., to suggest that the kaolinite formed through intensive alteration of an ultramafic protolith with neutral pH water, with the presence of spinel in some rocks suggesting incorporation of hydrothermally altered detrital ultramafic products (Royer et al., 2024).

Because erosion and transport has removed these rocks from their stratigraphic context, their formation is unclear. The Perseverance rover may have the opportunity to sample the kaolinite in the outer Jezero Crater rim for return to Earth (Figure 12). Optical petrology of samples could determine if they show pyroclastic textures or evidence of sedimentary transport. Scanning electron microscopy could be used to generate spatially-

resolved maps of element abundance and show if the remaining unaltered, non-phylllosilicate component of the rock is a better match for an Al/ Si-rich ash or an ultramafic composition. Additionally, this method could map and quantify Ni in the altered or unaltered portion of the sample and better measure the abundance and distribution of S, both of which would provide evidence for the pH of the altering fluid. Such detailed laboratory analysis could help determine whether these kaolinite-bearing rocks are the most intensively aqueously altered material thus far detected on Mars, as has been proposed (Royer et al., 2024) or could instead suggest that there was alteration of laterally extensive Al/ Si-rich pyroclastic deposits, either of which provides insight into Mars's past climate and evolution. Such sampling and sample return should be a priority.

5.5 Nature of alteration: Nili Fossae compared to Mawrth Vallis and Terra Sirenum

Nili Fossae, Mawrth Vallis, and Terra Sirenum share similarities in their mineralogy and stratigraphy. All three regions show Al-phylllosilicate consistently overlying Fe/Mg-phylllosilicate with associated sulfates in the jarosite–alunite solid solution, but there are distinctions between them that point to different local geologic processes.

The Mawrth Vallis Al-phylllosilicate deposits are composed of a lower unit of montmorillonite and an upper unit of kaolinite, both likely mixed with a hydrated silica component (Bishop et al., 2008). This Al-phylllosilicate-bearing unit is draped over the underlying Fe/Mg-phylllosilicate (Wray et al., 2008). This apparent draping and the 10s of m thickness of these units has been interpreted to indicate Al-phylllosilicate formation through extensive top-down pedogenic leaching (Klidas et al., 2025), but this stratigraphy is also consistent with an airfall deposit of a fine-grained pyroclastic deposit like a tephra or ash (Wray et al., 2008; Michalski et al., 2013; Klidas et al., 2025). The interpretation of Al-phylllosilicate draping underlying terrain was made for limited exposures in other regions of Mars but was not extended to most of Nili Fossae (Klidas et al., 2025).

A pyroclastic origin for the Al-phyllsilicate in Mawrth Vallis is also supported by the detection of the hydrated silica minerals allophane and imogolite above the kaolinite-bearing unit (Bishop and Rampe, 2016). These minerals form terrestrially during the early stages of weathering of volcanic ashes at pH of around 5–7 (Parfitt, 2009; Shoji et al., 1993; Wada, 1987).

A small number of jarosite deposits have been detected overlying the Mawrth Vallis Al-phyllsilicate-bearing unit and may have formed from the alteration of Fe-bearing phases stratigraphically above the Al-phyllsilicate (Farrand et al., 2009; Michalski et al., 2013; Farrand et al., 2014). Acidic fluids enriched in S from dissolution of volcanic gases or ash may have produced jarosite in small surface ponds (Farrand et al., 2009). Jarosite has also been found mixed with Al-phyllsilicate in limited locations in Mawrth Vallis (Bishop et al., 2020), similar to what we observe in Nili Fossae.

The weathering in Mawrth Vallis is thought to have been caused by surface water, as phyllosilicates and jarosite are found at varying elevations throughout the region (Michalski et al., 2013). The source of this water may have been from rainfall or an influx of ice/snow melt caused by brief climate excursions (Michalski et al., 2013; Bishop and Rampe, 2016).

The Terra Sirenum region contains two types of Al-phyllsilicate deposits: thin Al-phyllsilicate units within Eridania Basin and thick (60–150+ m) Al-phyllsilicate layered deposits outside of the basin (Leask et al., 2024). Eridania is a purported ancient sea on the edge of Terra Sirenum (Irwin et al., 2004) that contains possible localized marine hydrothermal minerals including phyllosilicates, carbonates, and sulfides (Hughes et al., 2024). Jarosite is associated with Fe/Mg-phyllsilicates in these deposits, likely formed from later alteration of Fe-sulfides under oxidizing conditions (Michalski et al., 2017). In the northern regions of Eridania, unlayered Al-phyllsilicate deposits including kaolinite, montmorillonite, and aluminous nontronite have been detected overlying Fe/Mg-phyllsilicates in altered Hesperian volcanic material filling the basin (Noe Dobrea et al., 2008). This has been interpreted as a pedogenic leaching sequence, as there is a diffuse contact with no clear textural distinction between these phyllosilicates (Adeli et al., 2015; Carter et al., 2015; Pajola et al., 2016; Leask et al., 2024). The presence of

associated jarosite and alunite largely in veins indicates acidic fluids and possible groundwater flow (Leask et al., 2024; Hughes et al., 2024).

In Terra Sirenum outside of Eridania basin, the Al-phyllsilicate is thought to have formed from a volcanic ash, similar to Nili Fossae and Mawrth Vallis. This is indicated by fine layers in the Al-phyllsilicate and diminishing thickness of the unit away from the volcano Arsia Mons (Leask et al., 2024). These Al-phyllsilicates are found across the region but are concentrated in Columbus and Cross craters. Columbus Crater contains widespread Al-phyllsilicate, largely kaolinite with some possible montmorillonite, associated with poly- and monohydrated sulfates, and one deposit of alunite. The Columbus Crater kaolinite may have formed from direct precipitation out of a deep paleolake, with alunite precipitating later from remnant shallow ponds (Wray et al., 2011). In Cross Crater, extensive alunite has been detected in association with kaolinite (Swayze et al., 2008). The alunite largely occurs in veins, suggesting possible alteration through the upwelling of acidic groundwater (Ehlmann et al., 2016). This groundwater may have become acidic through sulfur-enrichment from underground magma sources (Ehlmann et al., 2016, Leask et al., 2024). Little Fe/Mg-phyllsilicate is exposed outside of Eridania, though crater ejecta indicates its presence at depth beneath the Al-phyllsilicate unit in some locations (Leask et al., 2024).

In Nili Fossae, Mawrth Vallis, and Terra Sirenum, it appears that at least some of the observed Al-phyllsilicates formed from Al/Si-rich ash deposits with concurrent or subsequent precipitation of sulfates including jarosite and alunite. This creates similar mineralogy, but there are a few key differences between these sites. The Al-phyllsilicate in Nili Fossae appears to be dominantly kaolinite, while both Mawrth Vallis and Terra Sirenum have a mix of kaolinite and montmorillonite. This could suggest that Nili Fossae had more drainage during weathering to allow for the flushing of base cations including Ca^{2+} , Mg^{2+} , and Na^{+} , and/or the Al- and Si-rich protolith in this region had a lower concentration of these ions originally (Wilson, 2004). In Nili Fossae and Mawrth Vallis, the acidic sulfate that is formed within Al-phyllsilicate is jarosite as opposed to alunite as in Terra Sirenum. In Nili Fossae, we propose groundwater leached Fe out of the surrounding 100s of m thick Fe/Mg-phyllsilicate. This could explain the difference between Nili Fossae and Mawrth Vallis vs. Terra Sirenum. There may have been

insufficient Fe in the fluid in Terra Sirenum to produce jarosite rather than alunite. Fe oxide has been found alongside some of the Al-phyllsilicate in Mawrth Vallis (Wray et al., 2008), which suggests possibly more Fe in the original protolith or regions of Al-phyllsilicate lacking S. Further analysis is needed to determine the geochemical processes resulting in the difference in Fe oxide distribution.

5.6 Implications for regional chemistry and environmental conditions

There are no clear indicators of the pH of the fluid that formed the Al-phyllsilicates except for the scattered jarosite deposits that indicate localized acidic conditions. Kaolinite can form in a variety of pH environments, though the speed of its formation from feldspars is greatly enhanced by acidic alteration (Gíslason et al., 1996). There is no evidence of alunite in Nili Fossae, which is expected to form in oxidizing, Al-rich environments at low pH (pH 6.5–2.5 depending on the $\text{Al}^{3+}/\text{Fe}^{3+}$ ratio (Symonds et al., 1994; Poulet et al., 2009; Ehlmann et al., 2016)). Its absence despite the abundant kaolinite could suggest more neutral pH conditions throughout much of the region except where there was localized acidity. Experimental work shows that Mars' ancient denser CO_2 atmosphere likely produced widespread mildly acidic weathering conditions due to the formation of H_2CO_3 in water in contact with this atmosphere (Baron et al., 2019). Therefore, if the altering fluid that formed the Al-phyllsilicates was more neutral, it is possible that it either did not equilibrate with the CO_2 atmosphere or if it did, it was not sufficiently acidic to produce alunite. In the latter case, the mild acidity would still likely increase the rate of phyllsilicate formation (Kloprogge et al., 1999; Bandstra and Brantley, 2008).

No minerals were detected that necessarily indicate high temperature ($>100^\circ\text{C}$) conditions alongside the kaolinite in Nili Fossae. For example, kaolinite can be converted to zeolite through hydrothermal alteration (Gualtieri et al., 1997), but this mineral is not observed within the kaolinite deposits. We also do not detect other common metapelitic minerals including muscovite, biotite, staurolite, or cordierite (Hess, 1969). Other hydrothermal minerals including chlorite and prehnite, which form at temperatures $> 200^\circ\text{C}$ (Liou et al., 1983), are present to the southwest of the Nili Fossae rifts where they

co-occur with illite, but they remain distinct from the kaolinite deposits. Spinel, seen by the Perseverance Rover (Royer et al., 2024), is not detected. The lack of these high-temperature phases alongside kaolinite could suggest cold to moderate temperatures for kaolinite formation or that the abundance of hydrothermal minerals is small.

We can constrain the duration of aqueous activity required to produce the Al-phyllsilicates in this region. By mapping distances of Al-phyllsilicate units across Mars to fluvial geomorphic features such as valley network systems, Moore et al. (2025) conclude that these Al-phyllsilicate units form in regions where chemical weathering dominated over physical erosion processes. Bishop et al. (2018) model the duration of weathering required to produce an observed thickness of Fe/Mg-smectite on Mars under basic ($\text{pH} = 11$) conditions and low temperatures.

We apply this model to estimate the duration of weathering necessary to form the Nili Fossae kaolinite unit. We use the fast terrestrial weathering rate of 0.01 mm/year for the conversion of glassy ultramafic rock to dioctahedral phyllsilicate (Price et al., 2005). We chose a fast weathering rate due to the high alteration susceptibility of ash. We estimate a kaolinite content of 15%. With these assumptions, 3 million cumulative years of weathering over the ~ 3.7 billion year lifetime of the deposits would be required to produce ~ 130 m of kaolinite, the thickest deposit in Nili Fossae (Table 3). This is approximately an order of magnitude faster than the weathering that would be required to produce these units from a crystalline basaltic protolith (Price et al., 2005; Navarre-Sitchler and Brantley, 2007).

The aqueous alteration rate of primary minerals like feldspar and olivine is generally increased by higher temperatures or lower pH (Kloprogge et al., 1999; Bandstra and Brantley, 2008). Additionally, volcanic ashes weather substantially more rapidly than rock due to their high porosity and proportion of amorphous material (Aomine and Wada, 1962; Stefánsson and Gíslason, 2001; Ugolini and Dahlgren, 2002; Ye and Michalski, 2021). Further bounds on the temperature and pH of formation could be placed with Mars sample return and experiments on the alteration of ashes under Mars-like conditions. With these constraints, the weathering duration required to produce the kaolinite could be calculated with significantly less uncertainty. This would aid greatly in the understanding of Mars' early climate and hydrosphere.

The presence of jarosite helps constrain several aspects of the last stage of chemical weathering history in Nili Fossae. It indicates local acidity (pH of 1.5–4.5; Symonds et al., 1994; Poulet et al., 2009; Ehlmann et al., 2016), oxidizing conditions, and the presence of SO_4^{2-} in the fluids. Jarosite is a metastable phase. With continued contact with water at water/rock ratios of greater than 10, jarosite will eventually dissolve and reprecipitate as iron oxides/hydroxides including goethite ($\text{FeO}(\text{OH})$) and hematite (Fe_2O_3) (Zolotov and Shock, 2005). Therefore, the absence of iron oxides in kaolinite and the continued existence of jarosite suggests that it represents the final phase of substantial water interaction with rocks in this region.

6 Conclusions

Al-phyllsilicate is found throughout Nili Fossae, but it is concentrated around the fossae. Nearly all of the Al-phyllsilicate appears to be kaolinite with only 9 small deposits where other aluminosilicates are seen (which may be in mixture with kaolinite). High-resolution imagery typically shows a distinct difference in texture between the kaolinite (fine layering, polygonal fractures) and the underlying Fe/Mg-phyllsilicate (knobby, unlaminated, largely lacking polygonal fractures) that suggests that the kaolinite originated from a different protolith, transported sedimentary materials, as opposed to forming part of a continuous weathering sequence as they have been previously interpreted. This is supported by kaolinite's stratigraphic context, as it fills topographic lows in the underlying Fe/Mg-phyllsilicate on the local scale and is preferentially associated with large sedimentary basins on the regional scale. Due to the formation of Al-bearing phases without mixed Fe/Mg-phyllsilicate or Fe oxide, we conclude that the most likely protolith for this kaolinite is an Al- and Si-rich volcanic ash that was deposited across the region before it was reworked and accumulated in topographic lows. Alteration of the ash to kaolinite may have occurred syn- or post-deposition in sedimentary basins from either surface or groundwater.

Sparse, spatially restricted jarosite deposits occur across Nili Fossae in topographic lows in contact or mixed with kaolinite. We therefore conclude that jarosite precipitated from waters within the kaolinite protolith contemporaneously with or after

kaolinite formation. The requisite Fe to produce jarosite was likely provided by the altering fluid from leaching of the surrounding Fe/Mg-phylllosilicate, most likely groundwater due to the association of jarosite with topographic lows. The requisite S needed to create a highly acidic environment and produce sulfate was most likely sourced from S within the kaolinite protolith as jarosite is absent in the surrounding Fe/Mg phylllosilicate. These results help to place the aqueous alteration of Nili Fossae in context with similar jarosite-alunite solid solution in Al-phylllosilicates elsewhere on Mars. More Fe was available in Nili Fossae fluids leading to preferences for jarosite rather than alunite as in Terra Sirenum.

Additionally, the Perseverance Rover mission in Jezero Crater at the edge of Nili Fossae allows the opportunity to contextualize remote sensing data with recent rover observations. Collection and return to Earth for laboratory study would offer the opportunity to conclusively determine the chemical and environmental conditions of Al-phylllosilicate formation in Nili Fossae.

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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 used in Figures 3, 4, 6, and 7 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 used in Figure 4 are available from the NASA Planetary Data System

(<https://sites.brown.edu/relab/relab-spectral-database/>). Figures for this paper were generated with Python 3.8 and ArcGIS Pro. The Python code created for this project for automatic mineral identification is available at <https://caltech.box.com/s/a1vudj8ac5rgj3c17ovoa8q46fyiocgk>.

References

- Adeli, S., Hauber, E., Le Deit, L., & Jaumann, R. (2015). Geologic evolution of the eastern Eridania basin: Implications for aqueous processes in the southern highlands of Mars: Geologic evolution of the Eridania Basin. *Journal of Geophysical Research: Planets*, 120(11), 1774–1799. <https://doi.org/10.1002/2015JE004898>
- Alpers, C. N., Rye, R. O., Nordstrom, D. K., White, L. D., & King, B.-S. (1992). Chemical, crystallographic and stable isotopic properties of alunite and jarosite from acid—Hypersaline Australian lakes. *Chemical Geology*, 96(1–2), 203–226. [https://doi.org/10.1016/0009-2541\(92\)90129-S](https://doi.org/10.1016/0009-2541(92)90129-S)
- Aomine, S., & Wada, K. (1962). Differential weathering of volcanic ash and pumice, resulting in formation of hydrated halloysite. *American Mineralogist*, 47(9–10).
- Bishop, J. L., Dobrea, E. Z. N., McKeown, N. K., Parente, M., Ehlmann, B. L., Michalski, J. R., Milliken, R. E., Poulet, F., Swayze, G. A., Mustard, J. F., Murchie, S. L., & Bibring, J.-P. (2008). Phyllosilicate Diversity and Past Aqueous Activity Revealed at Mawrth Vallis, Mars. *Science*, 321(5890), 830–833. <https://doi.org/10.1126/science.1159699>
- Bishop, J. L., Fairén, A. G., Michalski, J. R., Gago-Duport, L., Baker, L. L., Velbel, M. A., Gross, C., & Rampe, E. B. (2018). Surface clay formation during short-term warmer and wetter conditions on a largely cold ancient Mars. *Nature Astronomy*, 2(3), 206–213. <https://doi.org/10.1038/s41550-017-0377-9>
- Bishop, J. L., & Rampe, E. B. (2016). Evidence for a changing Martian climate from the mineralogy at Mawrth Vallis. *Earth and Planetary Science Letters*, 448, 42–48. <https://doi.org/10.1016/j.epsl.2016.04.031>
- Bishop, J. L., Tirsch, D., Tornabene, L. L., Jaumann, R., McEwen, A. S., McGuire, P. C., Ody, A., Poulet, F., Clark, R. N., Parente, M., McKeown, N. K., Mustard, J. F., Murchie, S. L., Voigt, J., Aydin, Z., Bamberg, M., Petau, A., Michael, G., Seelos, F. P., ... Neukum, G. (2013). Mineralogy and morphology of geologic units at Libya Montes, Mars: Ancient aqueously derived outcrops, mafic flows, fluvial features, and impacts. *Journal of Geophysical Research: Planets*, 118(3), 487–513. <https://doi.org/10.1029/2012JE004151>

Bladh, K. W. (1982). The formation of goethite, jarosite, and alunite during the weathering of sulfide-bearing felsic rocks. *Economic Geology*, 77(1), 176–184. <https://doi.org/10.2113/gsecongeo.77.1.176>

Blesa, M. A., & Maroto, J. G. (1986). Dissolution of metal oxides. *Journal de Chimie Physique*, 83, 757–764. <https://doi.org/10.1051/jcp/1986830757>

Brantley, S. L., Bandstra, J., Moore, J., & White, A. F. (2008). Modelling chemical depletion profiles in regolith. *Geoderma*, 145(3–4), 494–504. <https://doi.org/10.1016/j.geoderma.2008.02.010>

Carr, M. H. (1995). The Martian drainage system and the origin of valley networks and fretted channels. *Journal of Geophysical Research: Planets*, 100(E4), 7479–7507. <https://doi.org/10.1029/95JE00260>

Carter, J., Loizeau, D., Mangold, N., Poulet, F., & Bibring, J.-P. (2015). Widespread surface weathering on early Mars: A case for a warmer and wetter climate. *Icarus*, 248, 373–382. <https://doi.org/10.1016/j.icarus.2014.11.011>

Catalano, J. G. (2013). Thermodynamic and mass balance constraints on iron-bearing phyllosilicate formation and alteration pathways on early Mars. *Journal of Geophysical Research: Planets*, 118(10), 2124–2136. <https://doi.org/10.1002/jgre.20161>

Chevrier, V., Poulet, F., & Bibring, J.-P. (2007). Early geochemical environment of Mars as determined from thermodynamics of phyllosilicates. *Nature*, 448(7149), 60–63. <https://doi.org/10.1038/nature05961>

Ehlmann, B. L., Mustard, J. F., Swayze, G. A., Clark, R. N., Bishop, J. L., Poulet, F., Des Marais, D. J., Roach, L. H., Milliken, R. E., Wray, J. J., Barnouin-Jha, O., & Murchie, S. L. (2009). Identification of hydrated silicate minerals on Mars using MRO-CRISM: Geologic context near Nili Fossae and implications for aqueous alteration. *Journal of Geophysical Research: Planets*, 114(E2), 2009JE003339. <https://doi.org/10.1029/2009JE003339>

Ehlmann, B.L., & Dundar, M. (2015, March 10 –16). *Are Noachian/Hesperian acidic waters key to generating Mars' regional-scale aluminum phyllosilicates? The importance of jarosite co-occurrences with Al-phyllosilicate units*. [Conference presentation abstract]. 46th Lunar and Planetary Science Conference. Houston, TX, United States. <https://www.hou.usra.edu/meetings/lpsc2015/pdf/1635.pdf>

Ehlmann, B. L., Swayze, G. A., Milliken, R. E., Mustard, J. F., Clark, R. N., Murchie, S. L., Breit, G. N., Wray, J. J., Gondet, B., Poulet, F., Carter, J., Calvin, W. M., Benzel, W. M., & Seelos, K. D. (2016). Discovery of alunite in Cross crater, Terra Sirenum, Mars: Evidence for acidic, sulfurous waters. *American Mineralogist*, 101(7), 1527–1542. <https://doi.org/10.2138/am-2016-5574>

Farley, K. A., Stack, K. M., Shuster, D. L., Horgan, B. H. N., Hurowitz, J. A., Tarnas, J. D., Simon, J. I., Sun, V. Z., Scheller, E. L., Moore, K. R., McLennan, S. M., Vasconcelos, P. M., Wiens, R. C., Treiman, A. H., Mayhew, L. E., Beyssac, O., Kizovski, T. V., Tosca, N. J., Williford, K. H., ... Zorzano, M.-P. (2022). Aqueously altered igneous rocks sampled on the floor of Jezero crater, Mars. *Science*, 377(6614), eabo2196. <https://doi.org/10.1126/science.abo2196>

Farrand, W. H., Glotch, T. D., & Horgan, B. (2014). Detection of copiapite in the northern Mawrth Vallis region of Mars: Evidence of acid sulfate alteration. *Icarus*, 241, 346–357. <https://doi.org/10.1016/j.icarus.2014.07.003>

Farrand, W. H., Glotch, T. D., Rice, J. W., Hurowitz, J. A., & Swayze, G. A. (2009). Discovery of jarosite within the Mawrth Vallis region of Mars: Implications for the geologic history of the region. *Icarus*, 204(2), 478–488. <https://doi.org/10.1016/j.icarus.2009.07.014>

Fassett, C. I., & Head, J. W. (2005). Fluvial sedimentary deposits on Mars: Ancient deltas in a crater lake in the Nili Fossae region. *Geophysical Research Letters*, 32(14), 2005GL023456. <https://doi.org/10.1029/2005GL023456>

Fawdon, P., Skok, J. R., Balme, M. R., Vye-Brown, C. L., Rothery, D. A., & Jordan, C. J. (2015). The geological history of Nili Patera, Mars. *Journal of Geophysical Research: Planets*, 120(5), 951–977. <https://doi.org/10.1002/2015JE004795>

Gaillard, F., & Scaillet, B. (2009). The sulfur content of volcanic gases on Mars. *Earth and Planetary Science Letters*, 279(1–2), 34–43. <https://doi.org/10.1016/j.epsl.2008.12.028>

Gaillard, F., Michalski, J., Berger, G., McLennan, S. M., & Scaillet, B. (2013). Geochemical Reservoirs and Timing of Sulfur Cycling on Mars. *Space Science Reviews*, 174(1–4), 251–300. <https://doi.org/10.1007/s11214-012-9947-4>

Gaudin, A., Decarreau, A., Noack, Y., & Grauby, O. (2005). Clay mineralogy of the nickel laterite ore developed from serpentinised peridotites at Murrin Murrin, Western Australia. *Australian Journal of Earth Sciences*, 52(2), 231–241. <https://doi.org/10.1080/08120090500139406>

Gaudin, A., Dehouck, E., & Mangold, N. (2011). Evidence for weathering on early Mars from a comparison with terrestrial weathering profiles. *Icarus*, 216(1), 257–268. <https://doi.org/10.1016/j.icarus.2011.09.004>

Gíslason, S. R., Arnorsson, S., & Armannsson, H. (1996). Chemical weathering of basalt in Southwest Iceland; effects of runoff, age of rocks and vegetative/glacial cover. *American Journal of Science*, 296(8), 837–907. <https://doi.org/10.2475/ajs.296.8.837>

Greenberger, R. N., Mustard, J. F., Kumar, P. S., Dyar, M. D., Breves, E. A., & Sklute, E. C. (2012). Low temperature aqueous alteration of basalt: Mineral assemblages of Deccan basalts and implications for Mars. *Journal of Geophysical Research: Planets*, 117(E11), 2012JE004127. <https://doi.org/10.1029/2012JE004127>

Gualtieri, A., Norby, P., Artioli, G., & Hanson, J. (1997). Kinetics of formation of zeolite Na-A [LTA] from natural kaolinites. *Physics and Chemistry of Minerals*, 24(3), 191–199. <https://doi.org/10.1007/s002690050032>

Hess, P. C. (1969). The metamorphic paragenesis of cordierite in pelitic rocks. *Contributions to Mineralogy and Petrology*, 24(3), 191–207. <https://doi.org/10.1007/BF00376047>

Hoefen, T. M., Clark, R. N., Bandfield, J. L., Smith, M. D., Pearl, J. C., & Christensen, P. R. (2003). Discovery of Olivine in the Nili Fossae Region of Mars. *Science*, 302(5645), 627–630. <https://doi.org/10.1126/science.1089647>

Hughes, E. B., Wray, J., Karunatillake, S., Fanson, G., Harrington, E., & Hood, D. R. (2024). Water-Limited Hydrothermalism and Volcanic Resurfacing of Eridania Basin, Mars. *Journal of Geophysical Research: Planets*, 129(7), e2024JE008461. <https://doi.org/10.1029/2024JE008461>

Irwin, R. P., Craddock, R. A., & Howard, A. D. (2005). Interior channels in Martian valley networks: Discharge and runoff production. *Geology*, 33(6), 489. <https://doi.org/10.1130/G21333.1>

Irwin, R. P., Howard, A. D., & Maxwell, T. A. (2004). Geomorphology of Ma'adim Vallis, Mars, and associated paleolake basins. *Journal of Geophysical Research: Planets*, 109(E12), 2004JE002287. <https://doi.org/10.1029/2004JE002287>

Jaumann, R., Neukum, G., Behnke, T., Duxbury, T. C., Eichentopf, K., Flohrer, J., Gasselt, S. v., Giese, B., Gwinner, K., Hauber, E., Hoffmann, H., Hoffmeister, A., Köhler, U., Matz, K.-D., McCord, T. B., Mertens, V., Oberst, J., Pischel, R., Reiss, D., ... Wählisch, M. (2007). The high-resolution stereo camera (HRSC) experiment on Mars Express: Instrument aspects and experiment conduct from interplanetary cruise through the nominal mission. *Planetary and Space Science*, 55(7–8), 928–952. <https://doi.org/10.1016/j.pss.2006.12.003>

Kerber, L., Forget, F., Madeleine, J.-B., Wordsworth, R., Head, J. W., & Wilson, L. (2013). The effect of atmospheric pressure on the dispersal of pyroclasts from martian volcanoes. *Icarus*, 223(1), 149–156. <https://doi.org/10.1016/j.icarus.2012.11.037>

Khuller, A. R., Kerber, L., Schwamb, M. E., Beer, S., Nogal, F. E., Perry, R., Hood, W., Aye, K.-M., Portyankina, G., & Hansen, C. J. (2022). Irregular polygonal ridge networks in ancient Noachian terrain on Mars. *Icarus*, 374, 114833. <https://doi.org/10.1016/j.icarus.2021.114833>

Klidaras, A., Navarre, R., Horgan, B., Farrand, W. H., Broz, A., Goudge, T. A., & Moore, R. (2025). Topography and mineralogy of clay deposits signify an epoch of warm and humid climate on early Mars. *Geology*, 53(5), 409–414.
<https://doi.org/10.1130/G52988.1>

Kloprogge, J. T., Komarneni, S., & Amonette, J. E. (1999). Synthesis of Smectite Clay Minerals: A Critical Review. *Clays and Clay Minerals*, 47(5), 529–554.
<https://doi.org/10.1346/CCMN.1999.0470501>

Kokaly, R., Clark, R.N., Swayze, G.A., Livo, K.E., Hoefen, T.M., Pearson, N.C., Wise, R.A., Benzal, W.N., Lowers, H.A., Driscoll, R.L., & Klein, A.J. (2017). *USGS Spectral Library Version 7 Data* [Dataset]. U.S. Geological Survey.
<https://doi.org/10.5066/F7RR1WDJ>

Le Deit, L., Flahaut, J., Quantin, C., Hauber, E., Mège, D., Bourgeois, O., Gurgurewicz, J., Massé, M., & Jaumann, R. (2012). Extensive surface pedogenic alteration of the Martian Noachian crust suggested by plateau phyllosilicates around Valles Marineris. *Journal of Geophysical Research: Planets*, 117(E11), 2011JE003983.
<https://doi.org/10.1029/2011JE003983>

Leask, E. K., Ehlmann, B. L., & Dundar, M. M. (2024). A 2-Billion-Year History of Water-Alteration in Terra Sirenum, Mars: Volcanism's Influence on Aluminum Clay Formation and Chemically Distinct Waters Forming Sulfates and Chlorides Into the Amazonian. *Journal of Geophysical Research: Planets*, 129(10), e2023JE008259.
<https://doi.org/10.1029/2023JE008259>

Liou, J. G., Kim, H. S., & Maruyama, S. (1983). Prehnite—Epidote Equilibria and their Petrologic Applications. *Journal of Petrology*, 24(4), 321–342.
<https://doi.org/10.1093/petrology/24.4.321>

Long, D. T., Fegan, N. E., McKee, J. D., Lyons, W. B., Hines, M. E., & Macumber, P. G. (1992). Formation of alunite, jarosite and hydrous iron oxides in a hypersaline system: Lake Tyrrell, Victoria, Australia. *Chemical Geology*, 96(1–2), 183–202.
[https://doi.org/10.1016/0009-2541\(92\)90128-R](https://doi.org/10.1016/0009-2541(92)90128-R)

Mandon, L., Quantin-Nataf, C., Thollot, P., Mangold, N., Lozac'h, L., Dromart, G., Beck, P., Dehouck, E., Breton, S., Millot, C., & Volat, M. (2020). Refining the age, emplacement and alteration scenarios of the olivine-rich unit in the Nili Fossae region, Mars. *Icarus*, 336, 113436. <https://doi.org/10.1016/j.icarus.2019.113436>

Mangold, N., Poulet, F., Mustard, J. F., Bibring, J. -P., Gondet, B., Langevin, Y., Ansan, V., Masson, Ph., Fassett, C., Head, J. W., Hoffmann, H., & Neukum, G. (2007). Mineralogy of the Nili Fossae region with OMEGA/Mars Express data: 2. Aqueous alteration of the crust. *Journal of Geophysical Research: Planets*, 112(E8), 2006JE002835. <https://doi.org/10.1029/2006JE002835>

Mavris, C., Cuadros, J., Nieto, J. M., Bishop, J. L., & Michalski, J. R. (2018). Diverse mineral assemblages of acidic alteration in the Rio Tinto area (southwest Spain): Implications for Mars. *American Mineralogist*, 103(12), 1877–1890. <https://doi.org/10.2138/am-2018-6330>

McEwen, A. S., Eliason, E. M., Bergstrom, J. W., Bridges, N. T., Hansen, C. J., Delamere, W. A., Grant, J. A., Gulick, V. C., Herkenhoff, K. E., Keszthelyi, L., Kirk, R. L., Mellon, M. T., Squyres, S. W., Thomas, N., & Weitz, C. M. (2007). Mars Reconnaissance Orbiter's High Resolution Imaging Science Experiment (HiRISE). *Journal of Geophysical Research: Planets*, 112(E5), 2005JE002605. <https://doi.org/10.1029/2005JE002605>

McSween, H. Y., Taylor, G. J., & Wyatt, M. B. (2009). Elemental Composition of the Martian Crust. *Science*, 324(5928), 736–739. <https://doi.org/10.1126/science.1165871>

Michalski, J. R., Dobrea, E. Z. N., Niles, P. B., & Cuadros, J. (2017). Ancient hydrothermal seafloor deposits in Eridania basin on Mars. *Nature Communications*, 8(1), 15978. <https://doi.org/10.1038/ncomms15978>

Michalski, J. R., Niles, P. B., Cuadros, J., & Baldrige, A. M. (2013). Multiple working hypotheses for the formation of compositional stratigraphy on Mars: Insights from the Mawrth Vallis region. *Icarus*, 226(1), 816–840. <https://doi.org/10.1016/j.icarus.2013.05.024>

Michalski, J. R., & Noe Dobrea, E. Z. (2007). Evidence for a sedimentary origin of clay minerals in the Mawrth Vallis region, Mars. *Geology*, 35(10), 951. <https://doi.org/10.1130/G23854A.1>

Milliken, R. (n.d.). *RELAB Spectral Library Bundle*. NASA Planetary Data System. <https://doi.org/10.17189/1519032>

Moore, J. M., & Howard, A. D. (2005). Large alluvial fans on Mars. *Journal of Geophysical Research: Planets*, 110(E4), 2004JE002352. <https://doi.org/10.1029/2004JE002352>

Moore, R. D., Goudge, T. A., Klidas, A., Horgan, B. H. N., Broz, A., Wordsworth, R., & Farrand, W. H. (2025). Deep chemical weathering on ancient Mars landscapes driven by erosional and climatic patterns. *Nature Astronomy*, 9(8), 1167–1175. <https://doi.org/10.1038/s41550-025-02584-w>

Murchie, S., Arvidson, R., Bedini, P., Beisser, K., Bibring, J. -P., Bishop, J., Boldt, J., Cavender, P., Choo, T., Clancy, R. T., Darlington, E. H., Des Marais, D., Espiritu, R., Fort, D., Green, R., Guinness, E., Hayes, J., Hash, C., Heffernan, K., ... Wolff, M. (2007). Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on Mars

Reconnaissance Orbiter (MRO). *Journal of Geophysical Research: Planets*, 112(E5), 2006JE002682. <https://doi.org/10.1029/2006JE002682>

Murchie, S., Roach, L., Seelos, F., Milliken, R., Mustard, J., Arvidson, R., Wiseman, S., Lichtenberg, K., Andrews-Hanna, J., Bishop, J., Bibring, J., Parente, M., & Morris, R. (2009). Evidence for the origin of layered deposits in Candor Chasma, Mars, from mineral composition and hydrologic modeling. *Journal of Geophysical Research: Planets*, 114(E2), 2009JE003343. <https://doi.org/10.1029/2009JE003343>

Mustard, J. F., Ehlmann, B. L., Murchie, S. L., Poulet, F., Mangold, N., Head, J. W., Bibring, J. -P., & Roach, L. H. (2009). Composition, Morphology, and Stratigraphy of Noachian Crust around the Isidis basin. *Journal of Geophysical Research: Planets*, 114(E2), 2009JE003349. <https://doi.org/10.1029/2009JE003349>

Mustard, J. F., Murchie, S. L., Pelkey, S. M., Ehlmann, B. L., Milliken, R. E., Grant, J. A., Bibring, J.-P., Poulet, F., Bishop, J., Dobrea, E. N., Roach, L., Seelos, F., Arvidson, R. E., Wiseman, S., Green, R., Hash, C., Humm, D., Malaret, E., McGovern, J. A., ... Wolff, M. (2008). Hydrated silicate minerals on Mars observed by the Mars Reconnaissance Orbiter CRISM instrument. *Nature*, 454(7202), 305–309. <https://doi.org/10.1038/nature07097>

Mustard, J. F., Poulet, F., Gendrin, A., Bibring, J.-P., Langevin, Y., Gondet, B., Mangold, N., Bellucci, G., & Altieri, F. (2005). Olivine and Pyroxene Diversity in the Crust of Mars. *Science*, 307(5715), 1594–1597. <https://doi.org/10.1126/science.1109098>

Navarre-Sitchler, A., & Brantley, S. (2007). Basalt weathering across scales. *Earth and Planetary Science Letters*, 261(1–2), 321–334. <https://doi.org/10.1016/j.epsl.2007.07.010>

Nesbitt, H. W., & Young, G. M. (1989). Formation and Diagenesis of Weathering Profiles. *The Journal of Geology*, 97(2), 129–147. <https://doi.org/10.1086/629290>

Noe Dobrea, E. Z., J. Moore, A. Howard, D. Catling, and J. Grant (2008, December 15–19), *Spectral and geomorphic evidence for a past inland sea in Eridania Basin, Mars*. [Conference presentation abstract]. American Geophysical Union Fall Meeting. San Francisco, CA, United States. <https://ui.adsabs.harvard.edu/abs/2008AGUFM.P32B..03N/abstract>

Pajola, M., Rossato, S., Carter, J., Baratti, E., Pozzobon, R., Erculiani, M. S., Coradini, M., & McBride, K. (2016). Eridania Basin: An ancient paleolake floor as the next landing site for the Mars 2020 rover. *Icarus*, 275, 163–182. <https://doi.org/10.1016/j.icarus.2016.03.029>

Pan, L., Ehlmann, B. L., Carter, J., & Ernst, C. M. (2017). The stratigraphy and history of Mars' northern lowlands through mineralogy of impact craters: A comprehensive survey. *Journal of Geophysical Research: Planets*, 122(9), 1824–1854. <https://doi.org/10.1002/2017JE005276>

Pan, L., Quantin-Nataf, C., Mandon, L., Martinot, M., & Beck, P. (2021). Spectral endmember variability on hyperspectral datasets of a martian meteorite—Implications for planetary surfaces. *Icarus*, 370, 114656. <https://doi.org/10.1016/j.icarus.2021.114656>

Parfitt, R. L. (2009). Allophane and imogolite: Role in soil biogeochemical processes. *Clay Minerals*, 44(1), 135–155. <https://doi.org/10.1180/claymin.2009.044.1.135>

Pelkey, S. M., Mustard, J. F., Murchie, S., Clancy, R. T., Wolff, M., Smith, M., Milliken, R., Bibring,

J. -P., Gendrin, A., Poulet, F., Langevin, Y., & Gondet, B. (2007). CRISM multispectral summary products: Parameterizing mineral diversity on Mars from reflectance. *Journal of Geophysical Research: Planets*, 112(E8), 2006JE002831. <https://doi.org/10.1029/2006JE002831>

Poulet, F., Bibring, J.-P., Mustard, J. F., Gendrin, A., Mangold, N., Langevin, Y., Arvidson, R. E., Gondet, B., Gomez, C., & The Omega Team. (2005). Phyllosilicates on Mars and implications for early martian climate. *Nature*, 438(7068), 623–627. <https://doi.org/10.1038/nature04274>

Poulet, F., & Erard, S. (2004). Nonlinear spectral mixing: Quantitative analysis of laboratory mineral mixtures. *Journal of Geophysical Research: Planets*, 109(E2), 2003JE002179. <https://doi.org/10.1029/2003JE002179>

Poulet, F., Mangold, N., Platevoet, B., Bardintzeff, J.-M., Sautter, V., Mustard, J. F., Bibring, J.-P., Pinet, P., Langevin, Y., Gondet, B., & Aléon-Toppani, A. (2009). Quantitative compositional analysis of martian mafic regions using the MEx/OMEGA reflectance data. *Icarus*, 201(1), 84–101. <https://doi.org/10.1016/j.icarus.2008.12.042>

Price, J. R., Velbel, M. A., & Patino, L. C. (2005). Rates and time scales of clay-mineral formation by weathering in saprolitic regoliths of the southern Appalachians from geochemical mass balance. *Geological Society of America Bulletin*, 117(5), 783. <https://doi.org/10.1130/B25547.1>

Quinn, D. P., & Ehlmann, B. L. (2019). The Deposition and Alteration History of the Northeast Syrtis Major Layered Sulfates. *Journal of Geophysical Research: Planets*, 124(7), 1743–1782. <https://doi.org/10.1029/2018JE005706>

Roach, L. H., Mustard, J. F., Swayze, G., Milliken, R. E., Bishop, J. L., Murchie, S. L., & Lichtenberg, K. (2010). Hydrated mineral stratigraphy of Ius Chasma, Valles Marineris. *Icarus*, 206(1), 253–268. <https://doi.org/10.1016/j.icarus.2009.09.003>

Robbins, S. J., Achille, G. D., & Hynek, B. M. (2011). The volcanic history of Mars: High-resolution crater-based studies of the calderas of 20 volcanoes. *Icarus*, 211(2), 1179–1203. <https://doi.org/10.1016/j.icarus.2010.11.012>

Royer, C., Bedford, C. C., Johnson, J. R., Horgan, B. H. N., Broz, A., Forni, O., Connell, S., Wiens, R. C., Mandon, L., Kathir, B. S., Hausrath, E. M., Udry, A., Madariaga, J. M., Dehouck, E., Anderson, R. B., Beck, P., Beyssac, O., Clavé, É., Clegg, S. M., ... Maurice, S. (2024). Intense alteration on early Mars revealed by high-aluminum rocks at Jezero crater. *Communications Earth & Environment*, 5(1), 671. <https://doi.org/10.1038/s43247-024-01837-2>

Scheller, E. L., & Ehlmann, B. L. (2020). Composition, Stratigraphy, and Geological History of the Noachian Basement Surrounding the Isidis Impact Basin. *Journal of Geophysical Research: Planets*, 125(7), e2019JE006190. <https://doi.org/10.1029/2019JE006190>

Seelos, F. P., Seelos, K. D., Murchie, S. L., Novak, M. A. M., Hash, C. D., Morgan, M. F., Arvidson, R. E., Aiello, J., Bibring, J.-P., Bishop, J. L., Boldt, J. D., Boyd, A. R., Buczkowski, D. L., Chen, P. Y., Clancy, R. T., Ehlmann, B. L., Frizzell, K., Hancock, K. M., Hayes, J. R., ... Wolff, M. J. (2024). The CRISM investigation in Mars orbit: Overview, history, and delivered data products. *Icarus*, 419, 115612. <https://doi.org/10.1016/j.icarus.2023.115612>

Shoji, S., Dahlgren, R., & Nanzyo, M. (1993). Chapter 4 Classification of Volcanic Ash Soils. In *Developments in Soil Science* (Vol. 21, pp. 73–100). Elsevier. [https://doi.org/10.1016/S0166-2481\(08\)70265-4](https://doi.org/10.1016/S0166-2481(08)70265-4)

Smith, M. R., Bandfield, J. L., Cloutis, E. A., & Rice, M. S. (2013). Hydrated silica on Mars: Combined analysis with near-infrared and thermal-infrared spectroscopy. *Icarus*, 223(2), 633–648. <https://doi.org/10.1016/j.icarus.2013.01.024>

Squyres, S. W., Grotzinger, J. P., Arvidson, R. E., Bell, J. F., Calvin, W., Christensen, P. R., Clark, B. C., Crisp, J. A., Farrand, W. H., Herkenhoff, K. E., Johnson, J. R., Klingelhöfer, G., Knoll, A. H., McLennan, S. M., McSween, H. Y., Morris, R. V., Rice, J. W., Rieder, R., & Soderblom, L. A. (2004). In Situ Evidence for an Ancient Aqueous Environment at Meridiani Planum, Mars. *Science*, 306(5702), 1709–1714. <https://doi.org/10.1126/science.1104559>

Stefánsson, A., & Gíslason, S. (2001). Chemical weathering of basalts, Southwest Iceland: Effect of rock crystallinity and secondary minerals on chemical fluxes to the ocean. *American Journal of Science*, 301, 513–556.

Stoffregen, R. E. (1993). Stability relations of jarosite and natrojarosite at 150–250°C. *Geochimica et Cosmochimica Acta*, 57(11), 2417–2429. [https://doi.org/10.1016/0016-7037\(93\)90406-M](https://doi.org/10.1016/0016-7037(93)90406-M)

Stoiber, R. E., & Rose, W. I. (1974). Fumarole incrustations at active central american volcanoes. *Geochimica et Cosmochimica Acta*, 38(4), 495–516. [https://doi.org/10.1016/0016-7037\(74\)90037-4](https://doi.org/10.1016/0016-7037(74)90037-4)

Sun, V. (2017). *Clays and Opals on Mars: Implications for Water-Rock Interactions Through Time*. Ph.D. thesis, Brown University. <https://doi.org/10.7301/Z08G8J58>

Swayze, G.A., Ehlmann, B.L., Milliken, R.E., Poulet, F., Wray, J.J., Rye, R.O., Clark, R.N., Desborough, G.A., Crowley, J.K., Gondet, B., Mustard, J.F., Seelos, K.D., & Murchie, S.L. (2008, December 15–19). *Discovery of the acid-sulfate mineral alunite in Terra Sirenum, Mars, using MRO CRISM: Possible evidence for acid-saline lacustrine deposits?* [Conference presentation abstract]. American Geophysical Union Fall Meeting. San Francisco, CA, United States.
<https://ui.adsabs.harvard.edu/abs/2008AGUFM.P44A..04S/abstract>

Symonds, R. B., Rose, W. I., Bluth, G. J., & Gerlach, T. M. (1994). Volcanic-gas studies: Methods, results, and applications. *Mineralogical Society of America*, 30, 1-66.

Tanaka, K. L., Skinner, J. A., Hare, T. M., Joyal, T., & Wenker, A. (2003). Resurfacing history of the northern plains of Mars based on geologic mapping of Mars Global Surveyor data. *Journal of Geophysical Research: Planets*, 108(E4), 2002JE001908.
<https://doi.org/10.1029/2002JE001908>

Tarnas, J. D., Mustard, J. F., Lin, H., Goudge, T. A., Amador, E. S., Bramble, M. S., Kremer, C. H., Zhang, X., Itoh, Y., & Parente, M. (2019). Orbital Identification of Hydrated Silica in Jezero Crater, Mars. *Geophysical Research Letters*, 46(22), 12771–12782. <https://doi.org/10.1029/2019GL085584>

Taylor, P. S., & Stoiber, R. E. (1973). Soluble Material on Ash from Active Central American Volcanoes. *Geological Society of America Bulletin*, 84(3), 1031.
[https://doi.org/10.1130/0016-7606\(1973\)84%253C1031:SMOAF%253E2.0.CO;2](https://doi.org/10.1130/0016-7606(1973)84%253C1031:SMOAF%253E2.0.CO;2)

Thollot, P., Mangold, N., Ansan, V., Le Mouélic, S., Milliken, R. E., Bishop, J. L., Weitz, C. M., Roach, L. H., Mustard, J. F., & Murchie, S. L. (2012). Most Mars minerals in a nutshell: Various alteration phases formed in a single environment in Noctis Labyrinthus. *Journal of Geophysical Research: Planets*, 117(E11), 2011JE004028.
<https://doi.org/10.1029/2011JE004028>

Tornabene, L. L., Moersch, J. E., McSween, H. Y., Hamilton, V. E., Piatek, J. L., & Christensen, P. R. (2008). Surface and crater-exposed lithologic units of the Isidis Basin as mapped by coanalysis of THEMIS and TES derived data products. *Journal of Geophysical Research: Planets*, 113(E10), 2007JE002988.
<https://doi.org/10.1029/2007JE002988>

Tornabene, L. L., Watters, W. A., Osinski, G. R., Boyce, J. M., Harrison, T. N., Ling, V., & McEwen, A. S. (2018). A depth versus diameter scaling relationship for the best-preserved melt-bearing complex craters on Mars. *Icarus*, 299, 68–83.
<https://doi.org/10.1016/j.icarus.2017.07.003>

Ugolini, F. C., & Dahlgren, R. A. (n.d.). Soil development in volcanic ash. *Global Environmental Research - English Edition*, 6(2), 69–82.

Velde, B., & Meunier, A. (2008). *The Origin of Clay Minerals in Soils and Weathered Rocks*. Springer Berlin Heidelberg. <https://doi.org/10.1007/978-3-540-75634-7>

Viviano, C. E., Seelos, F. P., Murchie, S. L., Kahn, E. G., Seelos, K. D., Taylor, H. W., Taylor, K., Ehlmann, B. L., Wiseman, S. M., Mustard, J. F., & Morgan, M. F. (2014). Revised CRISM spectral parameters and summary products based on the currently detected mineral diversity on Mars. *Journal of Geophysical Research: Planets*, 119(6), 1403–1431. <https://doi.org/10.1002/2014JE004627>

Wada, K. (1987). Minerals formed and mineral formation from volcanic ash by weathering. *Chemical Geology*, 60(1–4), 17–28. [https://doi.org/10.1016/0009-2541\(87\)90106-9](https://doi.org/10.1016/0009-2541(87)90106-9)

Weitz, C. M., Bishop, J. L., Thollot, P., Mangold, N., & Roach, L. H. (2011). Diverse mineralogies in two troughs of Noctis Labyrinthus, Mars. *Geology*, 39(10), 899–902. <https://doi.org/10.1130/G32045.1>

Werner, S. C. (2005). Major aspects of the chronostratigraphy and geologic evolutionary history of Mars, Ph.D. thesis, Free Univ. of Berlin, Berlin.

Wichman, R. W., & Schultz, P. H. (1989). Sequence and mechanisms of deformation around the Hellas and Isidis Impact Basins on Mars. *Journal of Geophysical Research: Solid Earth*, 94(B12), 17333–17357. <https://doi.org/10.1029/JB094iB12p17333>

Wilson, M. J. (2004). Weathering of the primary rock-forming minerals: Processes, products and rates. *Clay Minerals*, 39(3), 233–266. <https://doi.org/10.1180/0009855043930133>

Wray, J. J., Ehlmann, B. L., Squyres, S. W., Mustard, J. F., & Kirk, R. L. (2008). Compositional stratigraphy of clay-bearing layered deposits at Mawrth Vallis, Mars. *Geophysical Research Letters*, 35(12), 2008GL034385. <https://doi.org/10.1029/2008GL034385>

Wray, J. J., Milliken, R. E., Dundas, C. M., Swayze, G. A., Andrews-Hanna, J. C., Baldridge, A. M., Chojnacki, M., Bishop, J. L., Ehlmann, B. L., Murchie, S. L., Clark, R. N., Seelos, F. P., Tornabene, L. L., & Squyres, S. W. (2011). Columbus crater and other possible groundwater-fed paleolakes of Terra Sirenum, Mars. *Journal of Geophysical Research*, 116(E1), E01001. <https://doi.org/10.1029/2010JE003694>

Ye, B., & Michalski, J. R. (2022). Chemical weathering over hundreds of millions of years of greenhouse conditions on Mars. *Communications Earth & Environment*, 3(1), 266. <https://doi.org/10.1038/s43247-022-00602-7>

Zimbelman, D. R., Rye, R. O., & Breit, G. N. (2005). Origin of secondary sulfate minerals on active andesitic stratovolcanoes. *Chemical Geology*, 215(1–4), 37–60. <https://doi.org/10.1016/j.chemgeo.2004.06.056>

Zolotov, M. Y., & Shock, E. L. (2005). Formation of jarosite-bearing deposits through aqueous oxidation of pyrite at Meridiani Planum, Mars. *Geophysical Research Letters*, 32(21), 2005GL024253. <https://doi.org/10.1029/2005GL024253>