

Remote Sensing Aqueous Surface
Processes on Planets Red and Blue:
From Chemical Weathering Mineralogy
on Mars to Water Temperature in
Alaska's Riverine Corridors

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ABSTRACT

Ever since satellites were first launched into space in the 1950s, they have been utilized for critical science on Earth and eventually, around other planets as well. In Chapters 2 and 3, we use hyperspectral imagery and other remotely sensed data to examine the formation of aluminum phyllosilicate on Mars. Al-phyllosilicates across Mars have been proposed to have formed from extensive water leaching of basalt, though regional-specific studies suggest diversity between Al-phyllosilicate-bearing regions. Considering this complexity, in Chapter 2, we reexamine Al-phyllosilicate and its associated minerals in the Nili Fossae region. Using hyperspectral imagery from the CRISM instrument, we used Gaussian fitting to automatically identify and map Al-phyllosilicate and its associated minerals. We find that in contrast to prior interpretations, the Al-phyllosilicate in Nili Fossae most likely formed from weathering of an aluminous volcanic ash rather than from extensive leaching of basalt. In Chapter 3, we expand this analysis to a global survey of 6 Al-phyllosilicate-bearing regions on Mars. We examine the composition and stratigraphy of each region to determine their weathering histories, and we compare the regions to place them in a global context. We find that most of the Al-phyllosilicate on Mars is more consistent with volcanic ash alteration rather than extensive basalt leaching, though some regions are more consistent with basalt leaching. We conclude that the Al-phyllosilicate on Mars did not all form from one process, and our results demonstrate the potential for less extensive alteration and more widespread ash-producing volcanism in Mars' history than previously thought. In addition to composition, remotely sensed data can also be used to measure temperature. In Chapter 4, we use surface temperature derived from Landsat satellite data to examine the spatial and seasonal patterns of river temperature in Arctic rivers and their surrounding floodplains. Water temperature in the Arctic is interwoven with numerous environmental processes and is responding rapidly to the changing climate, but it is poorly monitored. We demonstrate that the Landsat temperature dataset is accurate for application to Arctic river environments, and we generate and examine water temperature maps of the Yukon River watershed. With these, we show that satellite-based temperature measurements can and should be used to address critical environmental questions in this region.

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LIST OF ACRONYMS

ASTER. Advanced Spaceborne Thermal Emission and Reflectance Radiometer

CRISM. Compact Reconnaissance Imaging Spectrometer for Mars

CTX. Context Camera

DEM. Digital elevation model

EVI. Enhanced vegetation index

HiRISE. High Resolution Imaging Science Experiment.

LST. Land Surface Temperature.

mNDWI. Modified normalized difference water index

MOLA. Mars Orbital Laser Altimeter

MTRDR. Map projected targeted reduced data record

NDVI. Normalized difference vegetation index

OMEGA. Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité

USGS. United States Geological Survey

VNIR. Visible–near-infrared

INTRODUCTION

1 Introduction

Of the many methods that can be used to study the surface processes that were or are active on planetary surfaces, remote sensing has been an essential tool to examine these processes with a broad, regional- to global-scale view. Remote sensing is the process of gathering data about an environment from a distance, without the need to make physical contact. This includes data gathered by instruments on platforms like satellites, drones, and airplanes; and the various instruments can be used to collect visual, compositional, topographic, or thermal data. In this thesis, we apply these methods to examine the history of ancient aqueous alteration on Mars and the present conditions of water temperature in the Arctic here on Earth. We rely on satellite-based observations, which allow us insight into two locations that are challenging or nearly impossible to reach with in situ analysis. By combining the many types of data that can be gathered from orbit, we are able to delve deeply into the story of water on the surfaces of these two planets.

1.1 Phyllosilicates on Mars

Foundational questions about Mars that drive planetary science are about water: where and how much was present, over what distribution and time scales, and how it interacted with rock and the evolving climate. Early fly-by and orbital missions displayed geomorphology suggestive of a water-rich past for Mars. For example, channel and branching valley networks appear analogous to terrestrial river and drainage systems (Irwin et al., 2005; Carr, 1995), and there are sedimentological deposits comparable to terrestrial alluvial fans (Moore and Howard, 2005). These features have been found on some of the oldest surfaces on Mars, dating back to the Noachian period (>3.7 Gyr). The presence of past water was confirmed by geochemical data including the detection of

aqueous alteration minerals by the Mars Exploration Rovers (Squyres et al., 2004).

One type of key alteration mineral is phyllosilicates, also known as clay minerals. They have been detected across Mars by two satellite-based visible–near-infrared hyperspectral imagers: OMEGA (Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité) on board the Mars Express Orbiter and CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) on board the Mars Reconnaissance Orbiter (Poulet et al., 2005; Mustard et al., 2008). These phyllosilicates are predominantly Fe/Mg-phyllosilicates including smectites, chlorites, and serpentine, and their abundance across late Noachian – early Hesperian (~3.7 Ga) terrains indicates widespread aqueous alteration. Al-phyllosilicates including kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and montmorillonite ($((\text{Na},\text{Ca})_{0.3}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n(\text{H}_2\text{O}))$) have also been detected in more localized regions of the late Noachian surface stratigraphically overlying Fe/Mg-phyllosilicate.

Since their initial detection on Mars in 2005 (Poulet et al., 2005), Al-phyllosilicates have been used as an indicator for the nature of Mars’ aqueous alteration. There have been numerous studies at both the regional and the global scale on these Al-phyllosilicates and their possible formation processes. Al-phyllosilicates have been detected locally by rovers including by Opportunity in Endeavor crater (Arvidson et al., 2014), Spirit in the Columbia Hills (Clark et al., 2007), and by Perseverance in float rocks in Jezero Crater (Royer et al., 2024). These small-scale deposits are not visible from orbit and may represent formation through cm–m-scale processes. They stand in contrast to the Al-phyllosilicate units detected from orbit, which are often the spectrally-dominant mineral over 1s–100s km^2 .

Global, remote sensing-based studies tend to consider all of the large-scale Al-phyllosilicate-bearing units on Mars to have formed in a similar way: they argue that Al-phyllosilicate overlying Fe/Mg-phyllosilicate formed as part of a pedogenic leaching sequence from a basaltic protolith (e.g., Poulet et al., 2005; Carter et al., 2015; Moore et al., 2025; Klidas et al., 2025). Notably, this process requires an extensive amount of

aqueous alteration. However, region-specific studies have identified diversity between these Al-phyllsilicate bearing regions, and some studies have suggested alternative formation mechanisms beyond pedogenic leaching.

There are broadly two different endmember weathering scenarios that can produce Al-phyllsilicate overlying Fe/Mg-phyllsilicates at large-scale on Mars: (1) extensive alteration of a basaltic protolith or (2) alteration of a separate, more aluminous protolith overlying a basaltic protolith. Fe oxides are expected to form alongside Al-phyllsilicate (Nesbitt and Young, 1989; Gaudin et al., 2005; Greenberger et al., 2012) because Fe^{3+} is relatively immobile in weathering, at least under terrestrial conditions, and their absence can indicate reducing, acidic, or originally Fe-poor conditions (King and McSween, 2005; Tosca et al., 2004). In acidic alteration, sulfate hydroxides in the jarosite–alunite solid solution can form (Stoffregen, 1993). Each scenario produces characteristic mineral assemblages; thus, spectral and textural analysis of the present-day mineralogy can be used to help reverse-engineer the identity of the protolith and the geochemistry of the water that produced the weathering.

1.2 Summary of Chapters 2 and 3

In the first section of this thesis, we examine Al-phyllsilicate formation across Mars using remote sensing datasets. We combined hyperspectral visible–near-infrared imagery from the CRISM spectrometer with high-resolution imagery from HiRISE and the Mars Context Camera and with digital elevation models to understand the mineralogy of Al-phyllsilicate alteration assemblages as well as their stratigraphy and geomorphic contexts. In chapter 2, we examine in detail the Al-phyllsilicate in Nili Fossae, a region of ancient terrain west of Mars’ Isidis impact basin. The Al-phyllsilicate in this region has previously been reported to have formed as part of a pedogenic leaching sequence (Ehlmann et al., 2009), but this analysis was performed without the most recent CRISM and HiRISE images and prior to the detection of jarosite alongside some of these Al-phyllsilicates (Ehlmann and Dundar, 2015). We developed a pipeline for using Gaussian

fitting to automatically detect and map phases of interest including Al-phyllsilicate, Fe/Mg-phyllsilicate, jarosite, alunite, hydrated silica, and Fe oxide. By examining our mineral maps and the available high-resolution imagery, we conclude that the Al-phyllsilicate in this region is not consistent with formation from leaching of basalt but rather is more consistent with formation from a reworked aluminous volcanic ash deposit, with jarosite forming from local, likely volcanically-sourced sulfur.

In chapter 3, we apply our methods to a global survey of Al-phyllsilicate-bearing regions. There have been numerous regional-scale studies of Al-phyllsilicate-bearing regions (e.g. Ehlmann et al., 2009; Le Deit et al., 2012; Bishop et al., 2013; Leask et al., 2024; Wray et al., 2008; Michalski et al., 2013; Bishop et al., 2020), and they have identified diversity and complexity in the Al-phyllsilicate formation. However, most global-scale studies largely continue to consider Al-phyllsilicate an indicator of extensive pedogenic leaching of basalt (e.g. Carter et al., 2015; Klidas et al., 2025; Moore et al., 2025). We perform a global analysis of these minerals, applying the same methods we used on a regional scale everywhere so that comparison can be rigorous and equitable. We examine six regions: Nili Fossae, Libya Montes, Hellas Planitia, Terra Sirenum, Valles Marineris, Mawrth Vallis. We use our Gaussian fitting pipeline to identify and map the same key minerals in all of these regions and examine their stratigraphy using high resolution imagery. We find that the Al-phyllsilicate in Hellas Planitia and Eridania Basin within Terra Sirenum are most consistent with formation from leaching of basalt. We find that Al-phyllsilicate in Nili Fossae, Libya Montes, Terra Sirenum, and Valles Marineris is instead more consistent with formation from alteration of an aluminous volcanic ash. Mawrth Vallis shows evidence of both processes. With this, we demonstrate that Al-phyllsilicate on Mars does not all form through the same process, nor does it always indicate extensive chemical alteration. Instead, our results suggest that limited weathering may have formed most of these deposits, and ash-producing volcanism may be more extensive than previously thought.

1.3 Arctic riverine corridor temperature

Today, Arctic environments exist in a precarious balance on the front lines of global climate change. Due to Arctic amplification, this region is experiencing more rapid warming than anywhere else on the planet, with an increase of up to 4°C predicted (Burn and Kokelj, 2009; Romanovsky et al., 2010; Post et al., 2019). This influence is felt everywhere in the region including by rivers and their surrounding wetlands. Rivers tie together numerous environments, processes, and water sources, all of which are influenced by the climate. In particular, the Arctic is a permafrost rich environment, but this permafrost is rapidly thawing due to climate change (Garnello et al., 2021; Schuur et al., 2022). As rivers navigate through permafrost-bearing terrain, they melt and erode it, so rivers influence the permafrost and in turn have their erosion style and speed stymied by it (Costard et al., 2003; Douglas et al., 2023; Geyman et al., 2024). Additionally, permafrost thaw and the formation of thermokarst lakes creates well-connected floodplains distinctive to these Arctic environments (Smith et al., 2005; Grosse et al., 2013).

Many of the questions about rivers and their riverine corridors in the Arctic, particularly in the changing climate, are tied to their temperature. This influences how they interact with permafrost during erosion (Costard et al., 2003; Douglas et al., 2023; Geyman et al., 2024), how inland waters release greenhouse gases (Striegl et al., 2012), and, critical to Arctic Indigenous communities, the health of salmon populations (Biela et al., 2022). While understanding the patterns of water temperature is essential to address these questions, the inland water temperature in these regions is not widely monitored. The United States Geological Survey (USGS) maintains a series of in situ temperature gauges in Alaska's rivers, but they are sparsely placed and cannot capture the diversity of water temperature across a river corridor (Krabbenhoft et al., 2022).

Thermal remote sensing can be used to address this gap. The Landsat satellites measure the radiance of energy emitted from the surface in the thermal infrared (~10–12 μm). This energy is proportional to temperature, and these data have been converted into the

Land Surface Temperature (LST) dataset (Cook et al., 2014). This dataset and other satellite-based thermal imaging has been commonly used to measure sea surface temperature and lake surface temperature, but it has been infrequently applied to rivers. In particular, this data type has not been applied to high-latitude environments that are affected by permafrost and large seasonal temperature swings. LST provides complete spatial coverage with a high temporal frequency (repeat rate of 1–7 days) and could be used to help address questions of river and wetlands temperature in remote but critical regions like Alaska.

1.4 Summary of Chapter 4

In chapter 4, we examine the spatial and seasonal patterns of water temperature in riverine corridors in Alaska using LST. We ground truth the LST data set by comparing surface temperature values from this dataset to contemporaneous temperature measurements taken by the USGS's in situ temperature gauge at Pilot Station on the Yukon River. We find good agreement, with a mean LST offset of $+0.73^{\circ}\text{C}$. We combine LST with visible–near infrared Landsat spectra to identify water, create masks of solely water temperature, and we remove 3 pixels from all water body borders to reduce the effects of land surface and water mixing. This creates a minimum size of water body that we were able to examine with this method, >210 meters in width. We examined 3 diverse locations in the Yukon River watershed: the meandering Koyukuk tributary, the confluence of the Yukon and Tanana rivers, and a typical anastomosing stretch of the Yukon River. For each location, we create and examine a water temperature map from just after ice break up in the spring, the height of summer, and just before refreezing in the fall. We compare these data to in situ air temperature and river discharge as well as in situ field temperature measurements taken at depth. We find that the surface temperature of rivers measured by LST is representative of the water temperature at depth, though this is not the case for thermally stratified oxbow lakes. We also find that water temperature largely traces air temperature, but it shows deviations from this due to mixing with other water bodies or internally. Finally, we discuss how remote sensing of water temperature

can be applied to critical questions in Arctic environments including the survivability of salmon populations, riverbank erosion, and carbon cycling.

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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).

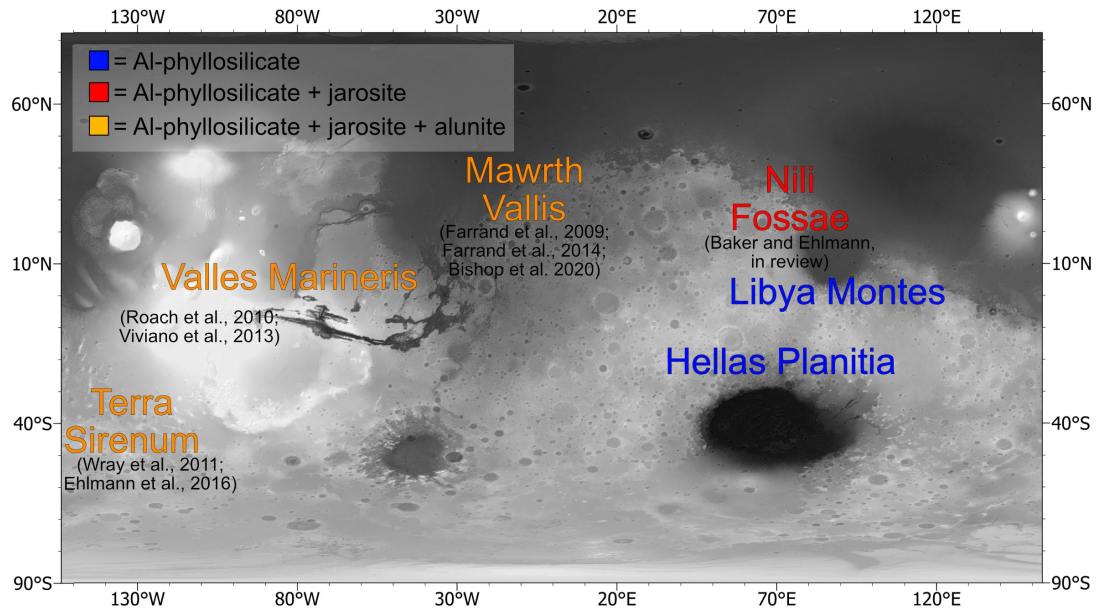


Figure 1: Global map of the six regions that contain Al-phyllsilicate-bearing units that appear to stratigraphically overlie Fe/Mg-phyllsilicate-bearing units (Carter et al., 2015). Colored circles indicate regions where nearby jarosite and/or alunite has been detected alongside Al-phyllsilicate.

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.

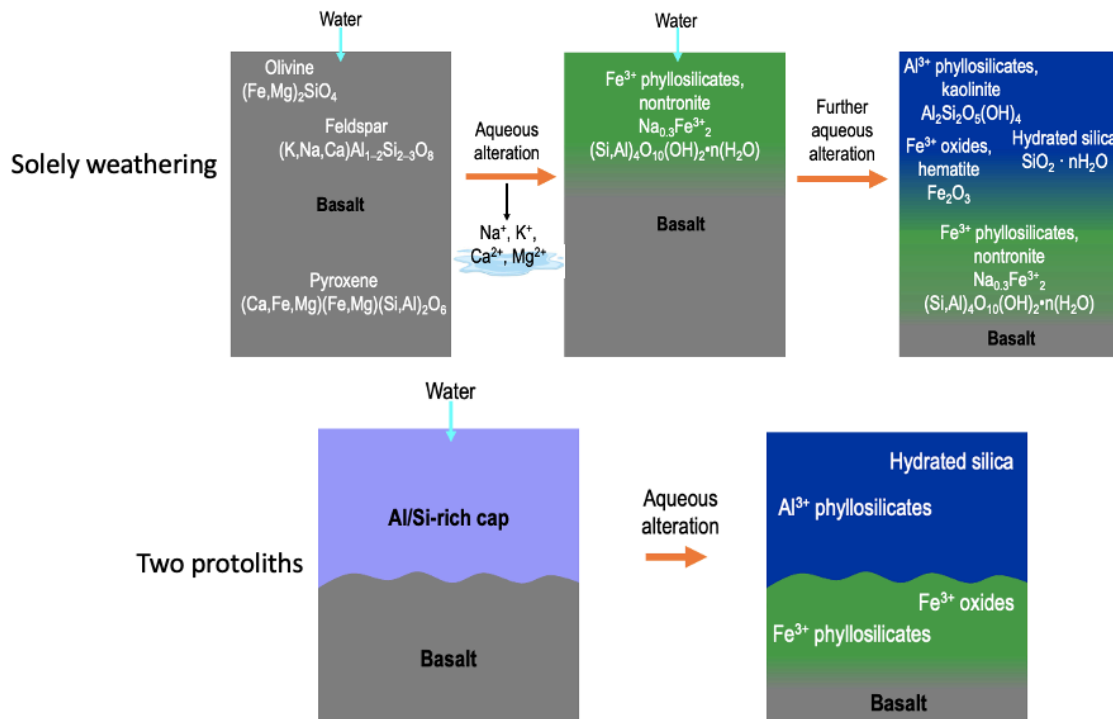


Figure 2: Possible endmember weathering scenarios for the formation of Al-phyllsilicate overlying Fe/Mg-phyllsilicate. a) Alteration of a basalt protolith under oxidizing, neutral-pH conditions. When water is added from the top down, first soluble cations such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} are leached from the system and Fe^{3+} 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-

phyllosilicate 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 phyllosilicates and alunite around Al-phyllosilicates (Leask et al., 2024). In Valles Marineris, some Al-phyllosilicate overlies Fe/Mg-phyllosilicate 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-phyllosilicate, with probable jarosite associated locally with Fe/Mg-phyllosilicate (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-phyllosilicates could suggest the formation of the Al-phyllosilicates by acidic weathering under oxidizing conditions or a later acidic overprinting process.

In this work, we examine the formation of Al-phyllosilicate in the region of Nili Fossae. The Al-phyllosilicate 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-phylosilicate-bearing units with all available high-resolution imagery. We begin by developing an automated pipeline to detect and map Al-phylosilicate 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-phyllosilicate, this algorithm selected Fe/Mg-phyllosilicate-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-phyllosilicate 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-phyllosilicate 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-phyllosilicates 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-phyllsilicates, Fe/Mg-phyllsilicates, 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	$(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2215	Al-OH vibrational
Fe/Mg-phyllsilicate	Nontronite	$\text{Na}_{0.3}\text{Fe}_2((\text{Si,Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2285	Fe-OH vibrational
	Saponite	$\text{Ca}_{0.25}(\text{Mg,Fe})_3((\text{Si,Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2315	Mg-OH vibrational
Sulfate group	Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	2265	Fe-OH vibrational
	Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$	2165	Al-OH vibrational
Hydrated silica	Opal	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	2210–2245 (broad)	Si-OH vibrational

Fe oxide/hydroxide	Hematite	Fe_2O_3	540	Fe electronic charge transfer
	Goethite	$\text{FeO}(\text{OH})$	490	Fe electronic charge transfer
	Ferrihydrite	$\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$	525	Fe electronic charge transfer
	Lepidocrocite	$\text{FeO}(\text{OH})$	490	Fe electronic charge transfer

Minerals targeted for identification by the Gaussian fitting algorithm and the wavelengths and causes of the diagnostic absorptions used by the algorithm for each mineral.

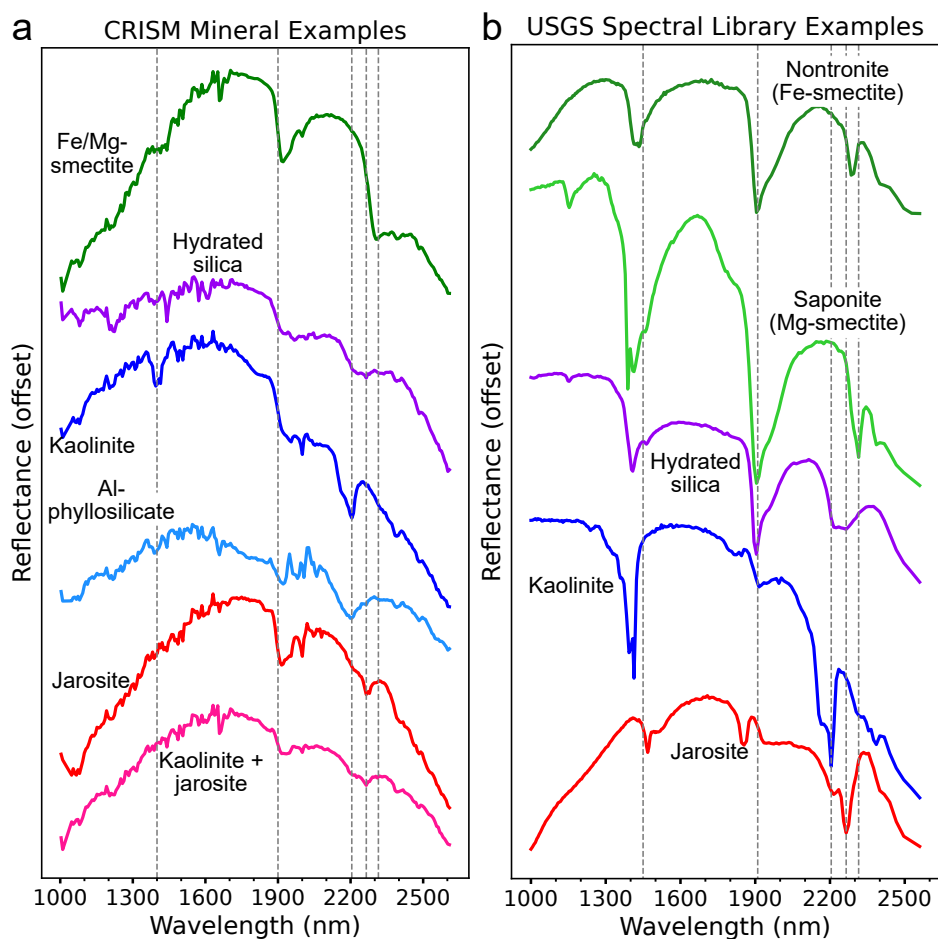


Figure 3: a) Representative examples of spectra from Nili Fossae CRISM MTRDR I/F images that contain alteration minerals. Each spectrum is the average of ~100 pixels from FRT0000A053 (Fe/Mg-smectite, kaolinite + jarosite), FRT000051EE (hydrated silica), FRT0000C202 (kaolinite), FRT00009971 (Al-phyllsilicate), 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- phyllosilicate , hydrated silica, alunite	1	Depth, center wavelength, width	N/A	2112.87 nm – 2331.02 nm	2159.83 nm – 2279.98 nm	BD2190 or BD2250 > 0.006 and LCPINDEX2 < 0.027 Once fit, exclude pixels with centers > 2250.02 nm
Fe/Mg- phyllosilicate	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 wavelengths	2112.87 nm – 2331.02 nm	Fixed at 2265.01 nm and 2205.07 nm	BD2265 > 0.003 and R2284.72 > R2264.88
Fe oxide	1	Depth, center wavelength, width	N/A	442 nm – 631 nm	400 nm – 600 nm	BD530 > 0.16, fit Gaussian depth > BD625

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.

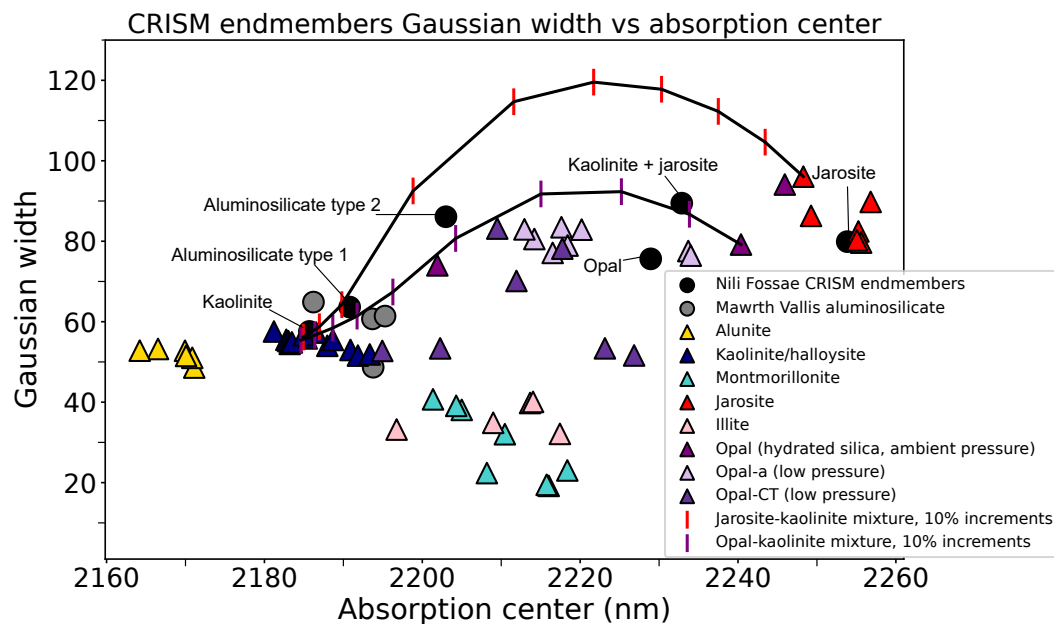


Figure 4: Gaussian-fit width vs. Gaussian-fit center wavelength for minerals with absorptions around 2200 nm and CRISM spectra around Nili Fossae. Also plotted are the same parameters for USGS and RELAB spectral library examples of minerals we

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-phyllsilicate 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-phylllosilicate 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.

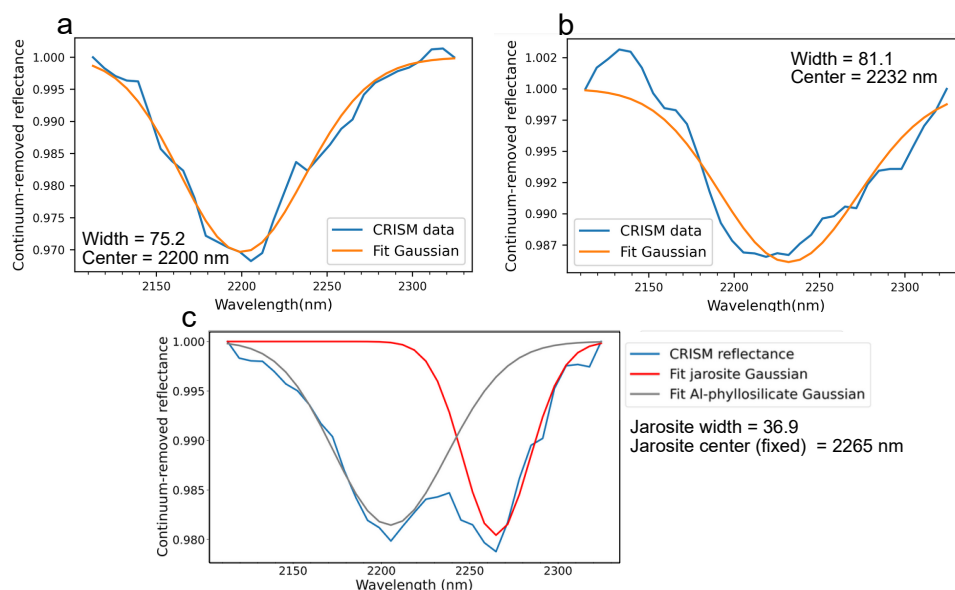


Figure 5: Examples of Gaussian curve fits to continuum-removed ratioed I/F spectra of a) kaolinite (from FRT0000A053), b) opal hydrated silica (from FRT000051EE), and c) kaolinite mixed with jarosite (from FRT0000A053). Note that the Gaussian curves do not perfectly fit the spectra, but the Gaussian 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.

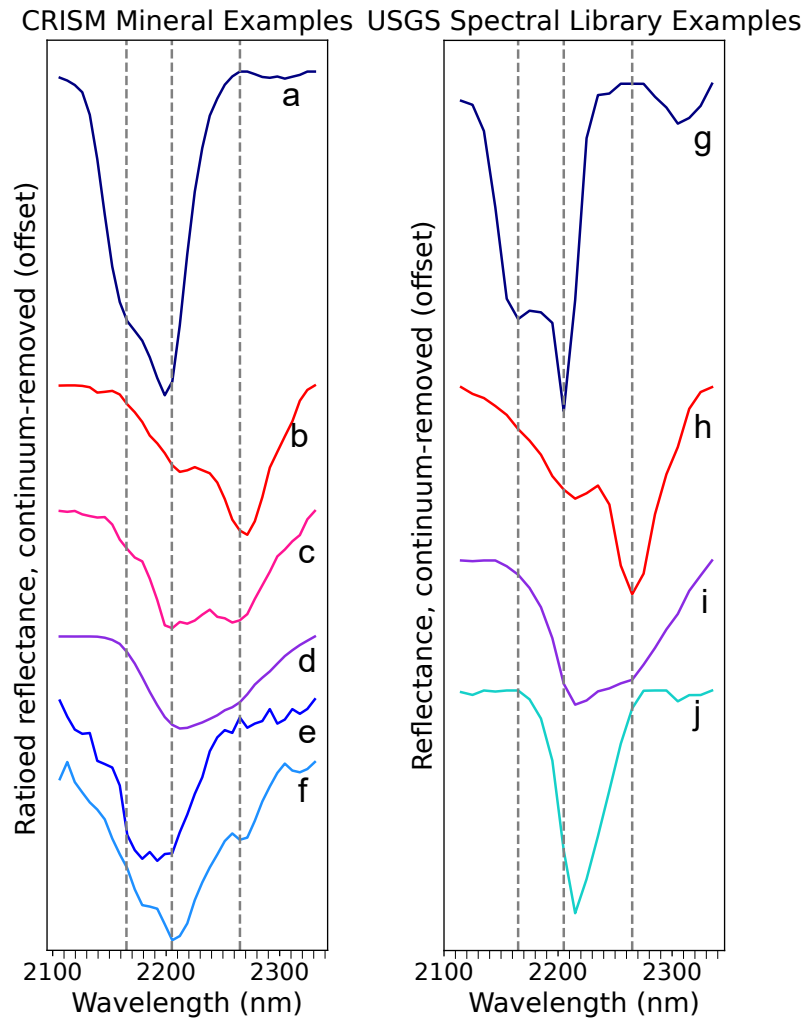


Figure 6: Representative examples of spectra with absorptions around 2200 nm that are observed in Nili Fossae. On the left are continuum-removed ratioed CRISM MTRDR I/F spectra. Each spectrum is the mean of an ROI with 30-1000 pixels. a) kaolinite (from C202, centered on point 155, 577), b) jarosite (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 lepidocrocite—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.

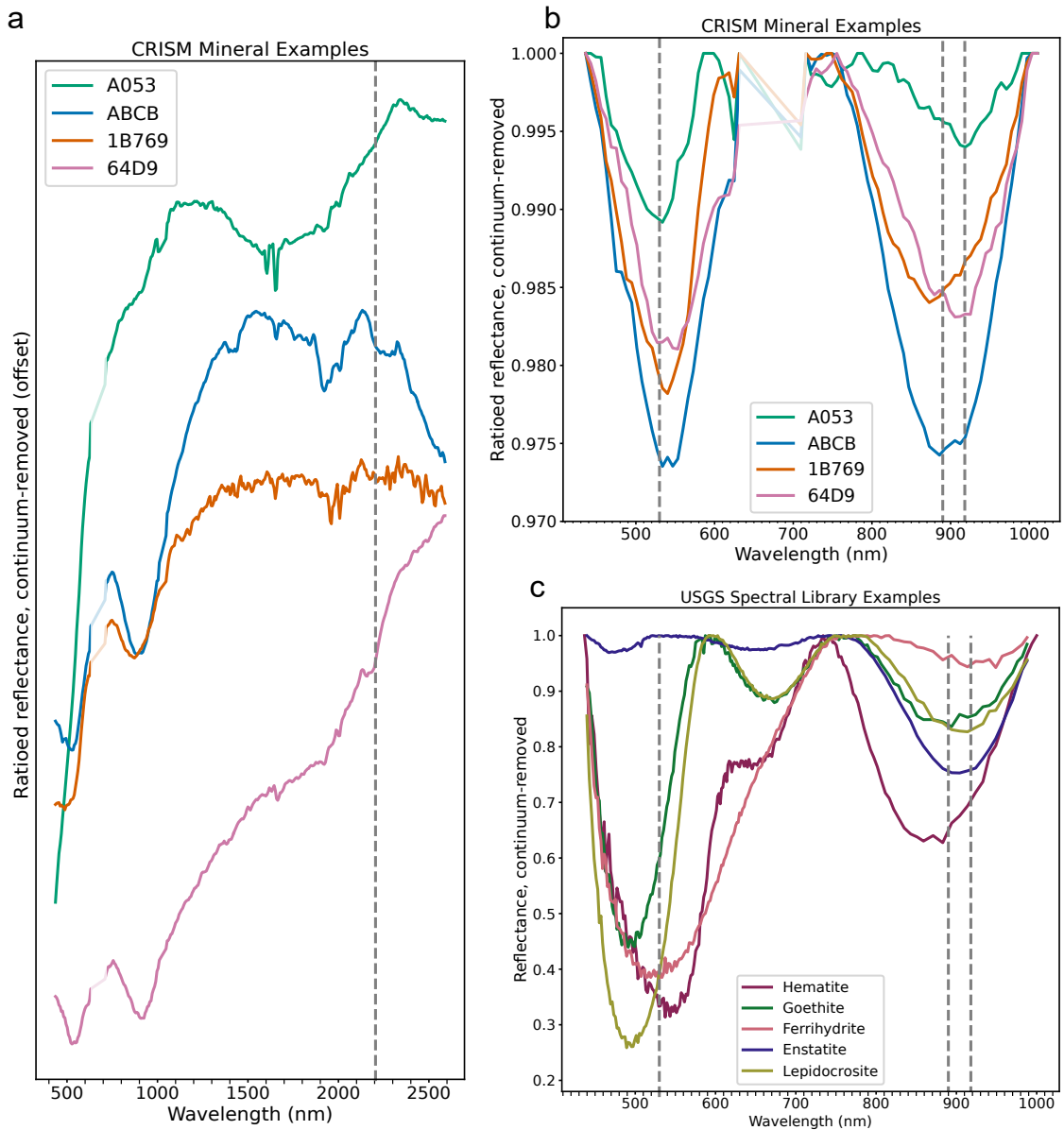


Figure 7: Representative examples of spectra of the minerals absorbing around 500 nm and 900 nm that are observed in Nili Fossae compared to laboratory samples. a) Full wavelength range ratioed CRISM MTRDR I/F spectra. Each spectrum is the mean of an ROI with 100s of pixels from A053, centered on point (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-phyllosilicate, 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).

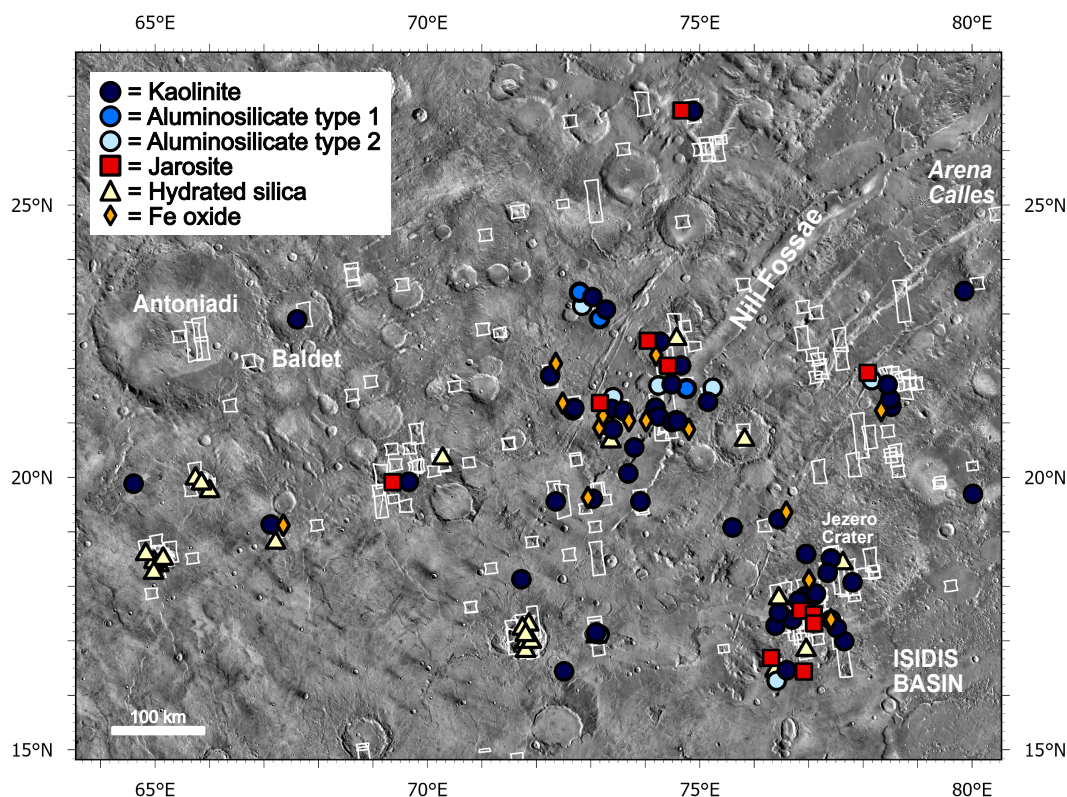


Figure 8: Distribution of detections of the alteration products kaolinite, hydrated aluminosilicate type 1 and 2 (as shown in Figure 6), jarosite, hydrated silica, and Fe oxide in Nili Fossae within CRISM MTRDR images (footprints in white). Basemap is THEMIS daytime infrared.

In agreement with prior findings (Ehlmann et al., 2009, Carter et al., 2015), kaolinite consistently occurs stratigraphically above adjacent Fe/Mg-phyllosilicate. 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.

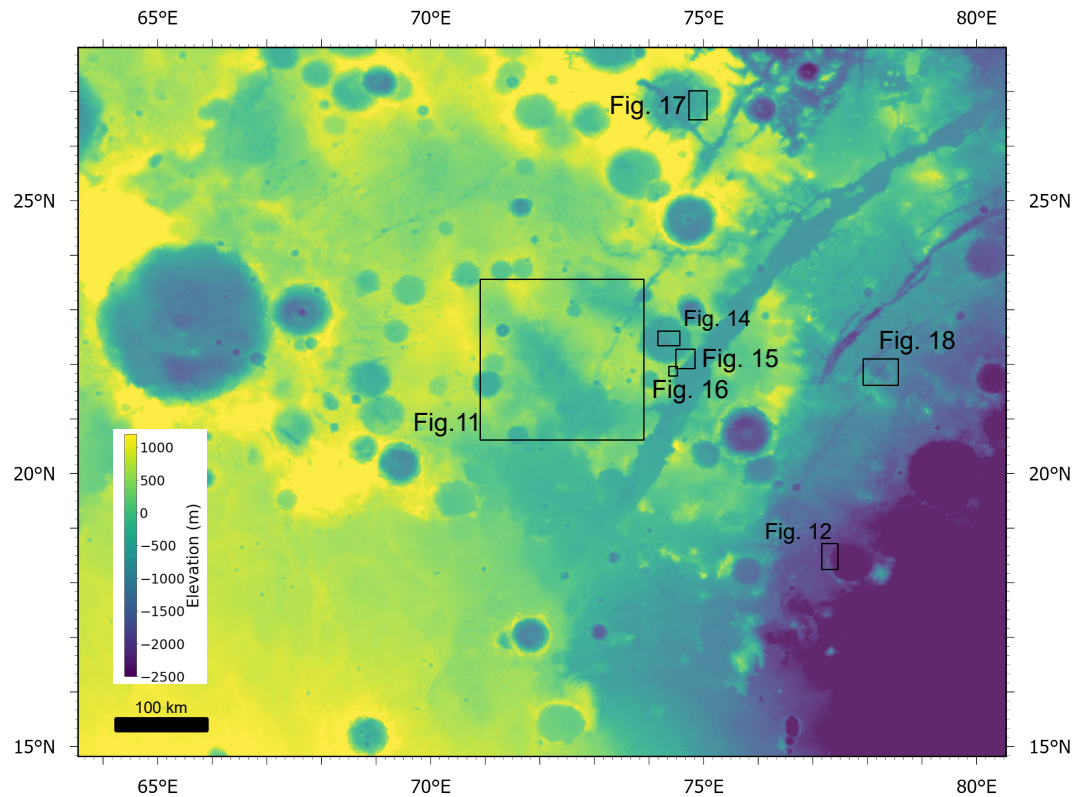


Figure 9: Locations of subsequent figures demonstrating their topographic context around Nili Fossae. Basemap is the MOLA 463 m DEM (USGS).

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).

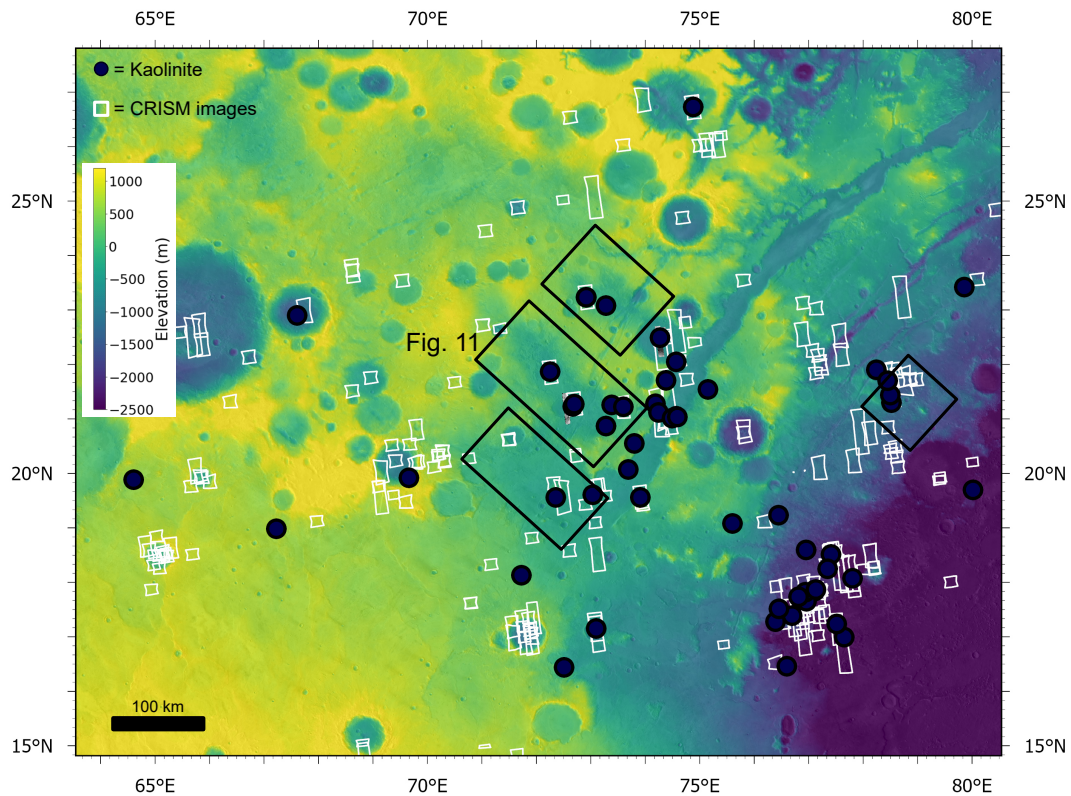


Figure 10: Topographic context of all kaolinite deposits in Nili Fossae. The boxes indicate four large eroded topographic lows that contain kaolinite as described in the text. Basemap is the MOLA 463 m DEM (USGS).

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-phyllosilicate. The depression has been partially filled with lava flows. Kaolinite and Fe/Mg-phyllosilicate 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).

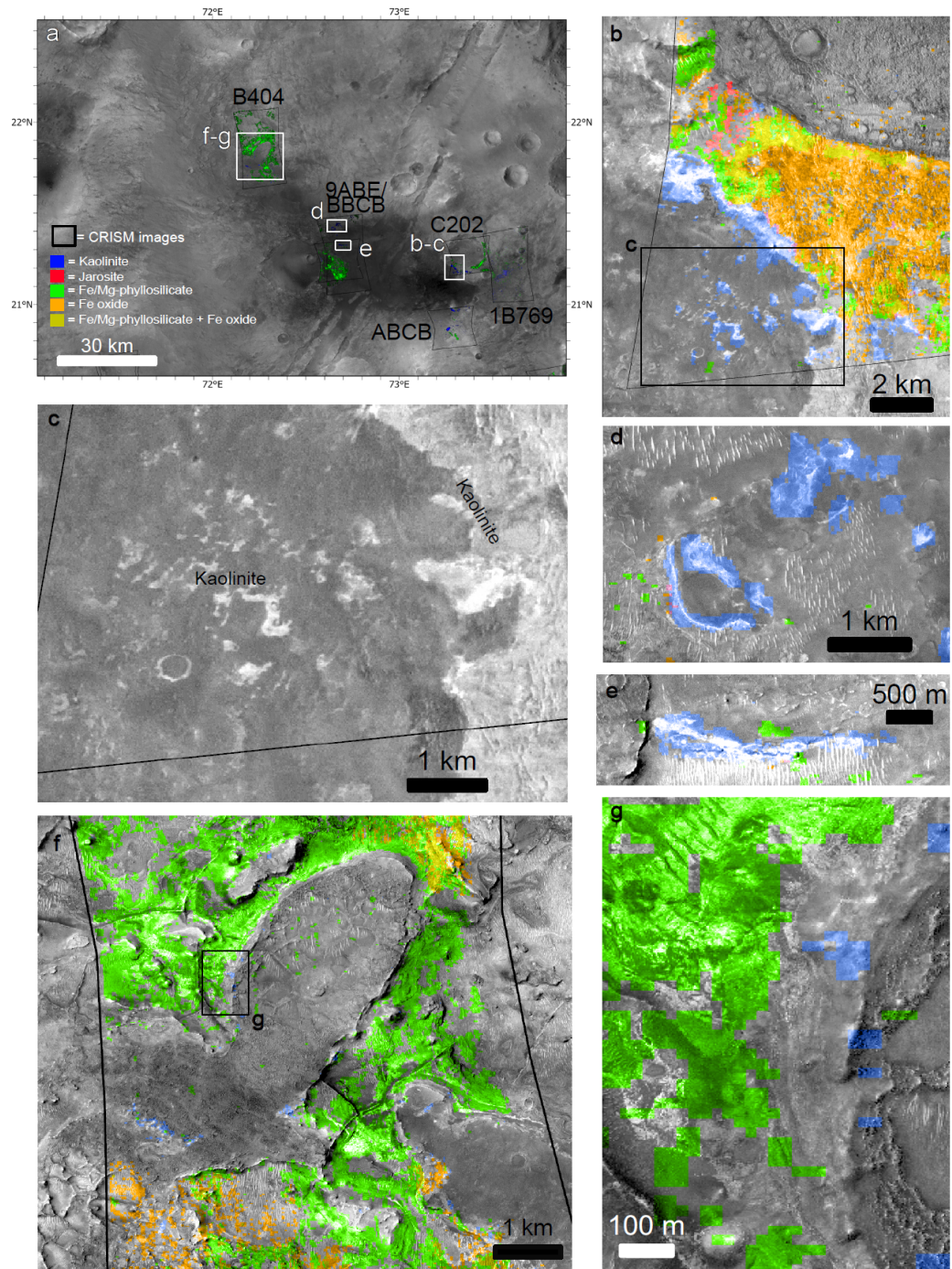


Figure 11: Kaolinite, jarosite, and Fe/Mg-phyllosilicate detections within a large erosional basin to the west of the fossae. a) The erosional basin in CTX. b) An example of the upper portion of the topographic low in image C202 demonstrating the contact between the phyllosilicate-bearing upper unit 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-phylllosilicate 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.

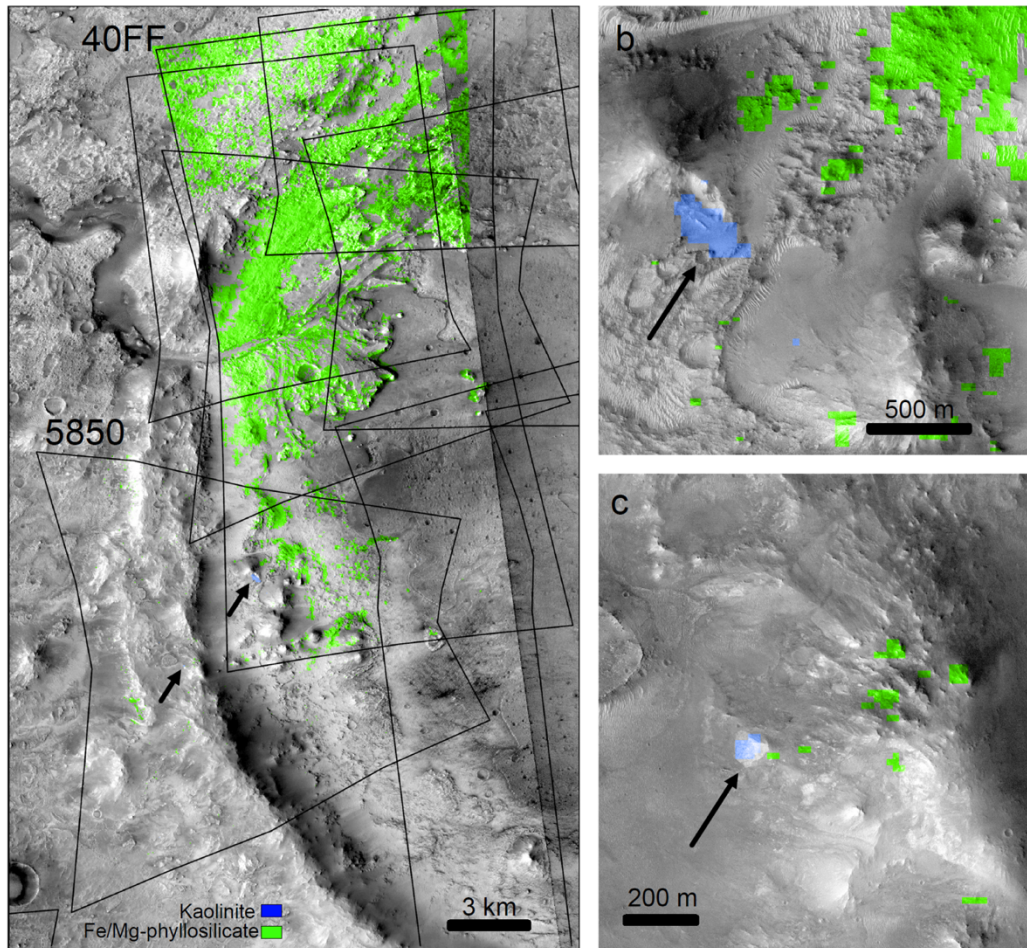


Figure 12: a) Al-phylosilicate and Fe/Mg-phylosilicate mineral map of the western fan of Jezero Crater on CTX imagery. Arrows point to the locations of kaolinite deposits in the crater rim unit, which are shown in more detail in HiRISE imagery in b and c.

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.

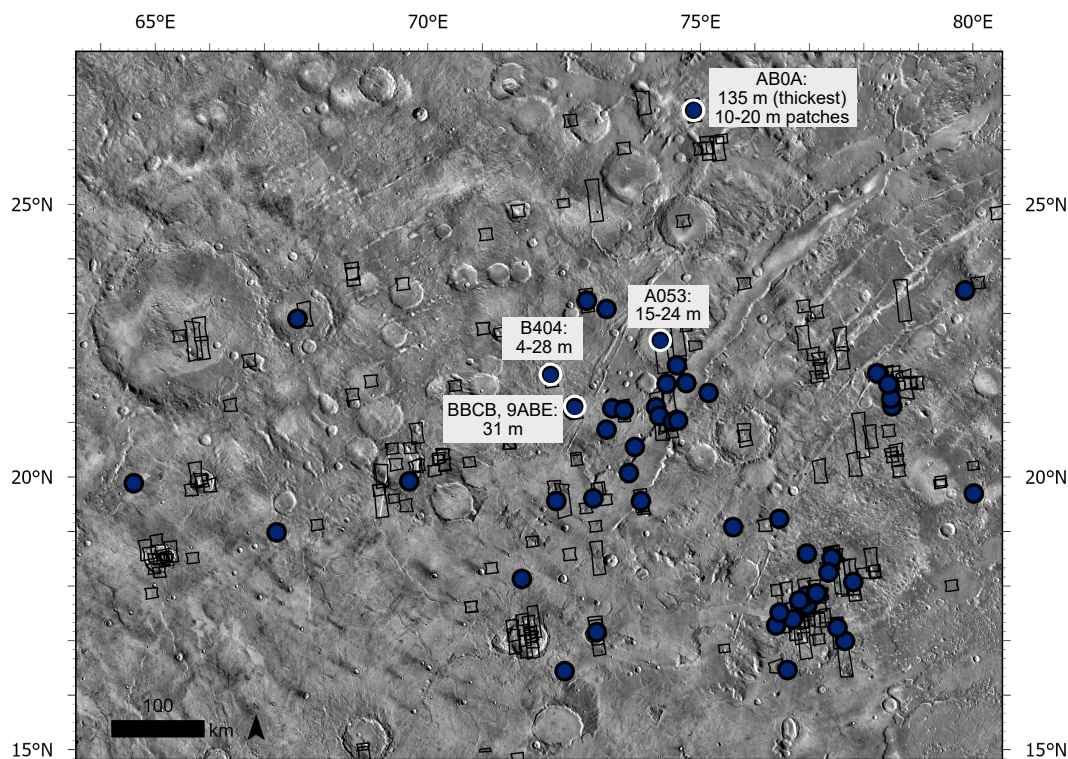


Figure 13: Locations of all Al-phylosilicate detections in Nili Fossae with apparent thicknesses marked for the few images where there was sufficient relief of the Al-phylosilicate deposits for thickness to be measurable in HRSC (BBCB, 9ABE, B404) and CTX (A053, AB0A) DEMs.

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-phyllosilicate 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-phyllosilicate 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-phyllosilicate. Fe oxide appears to be stratigraphically below the kaolinite and sometimes above Fe/Mg-phyllosilicate 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-phyllosilicate (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).

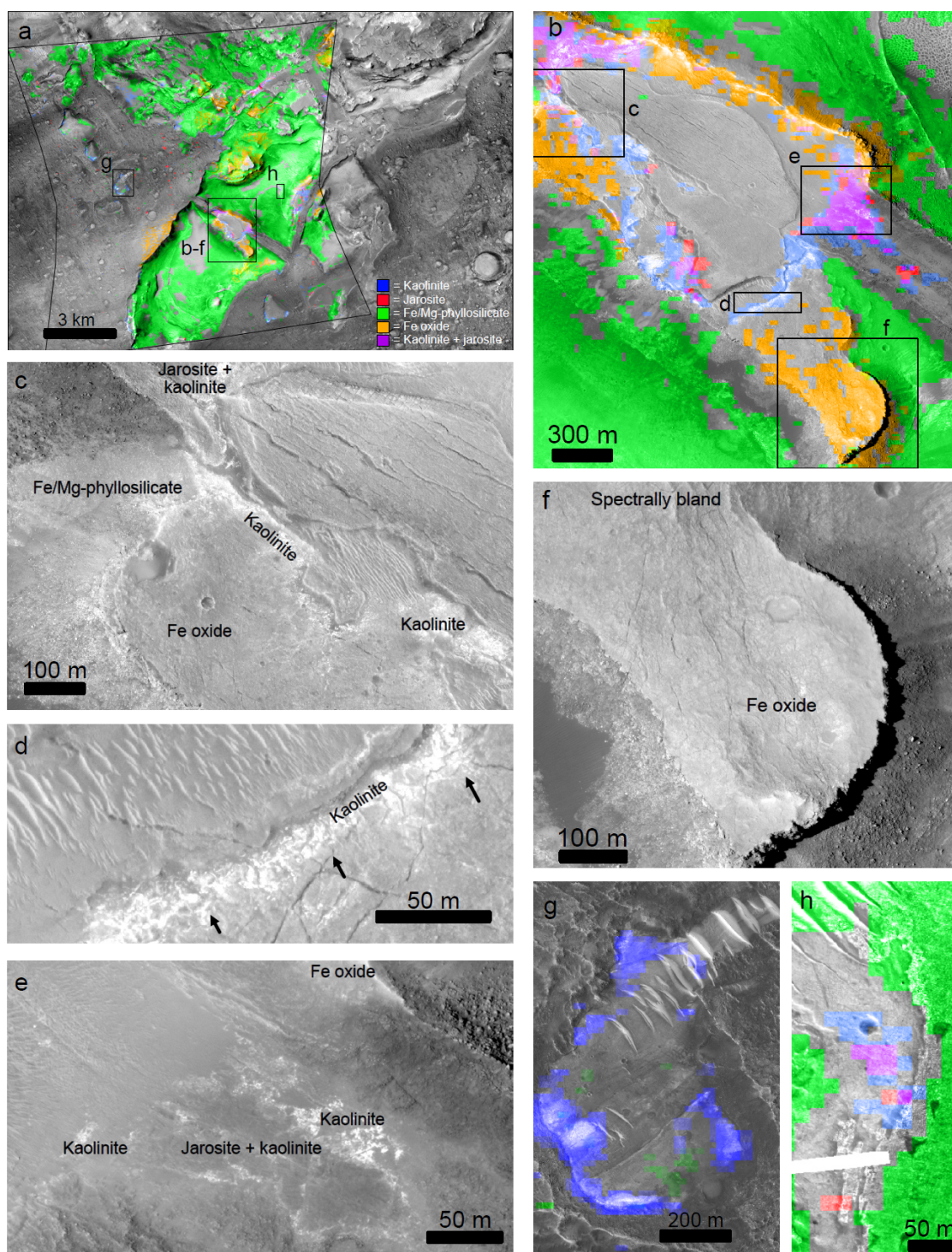


Figure 14: Kaolinite, Fe/Mg-phylllosilicate, and jarosite deposits in sedimentary fill in an impact crater next to the main Nili Fossae graben. a) The full mineral map of A053 with a CTX basemap. The large pit carved from aeolian erosion exposes ~300 m of Fe/Mg-

phyllosilicate, 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.

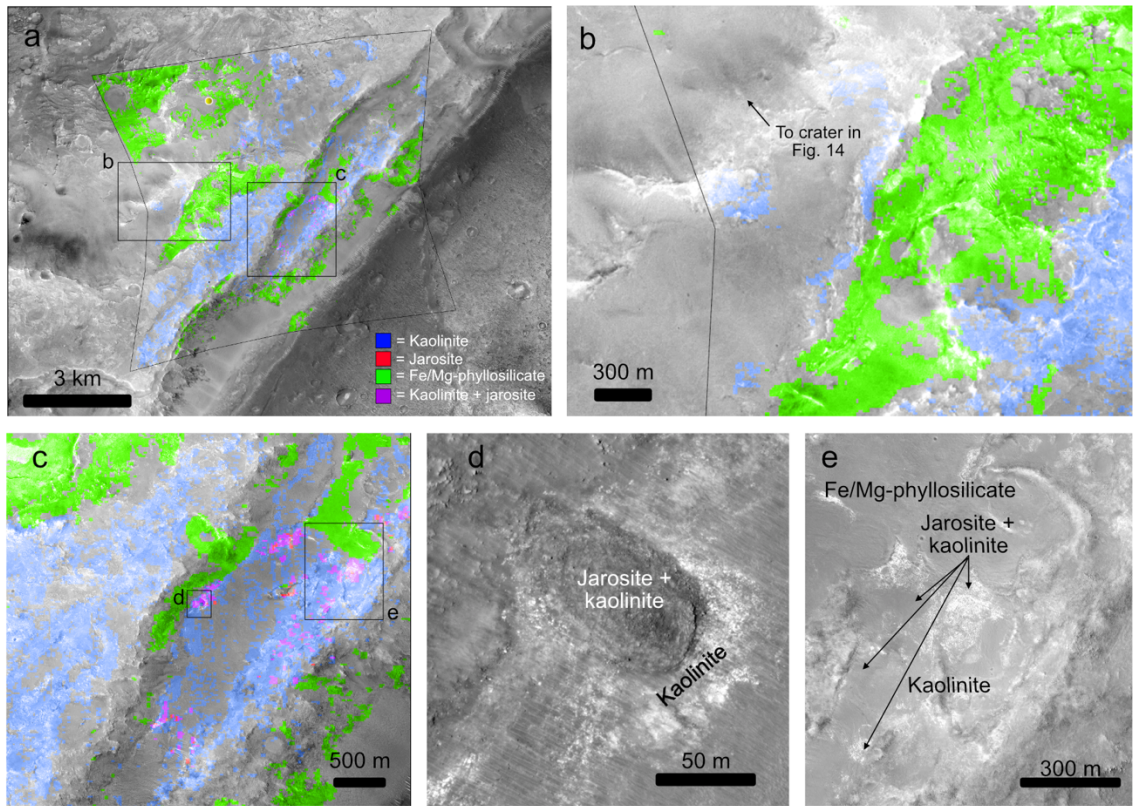


Figure 15: a) The full mineral map of the image FRT00009971 showing kaolinite, Fe/Mg-phyllosilicate, and jarosite on the edge of the main trough and the adjacent crater containing image A053 as shown in Figure 14. b) Some of the kaolinite is exposed along with Fe/Mg-phyllosilicate in the crater wall. 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).

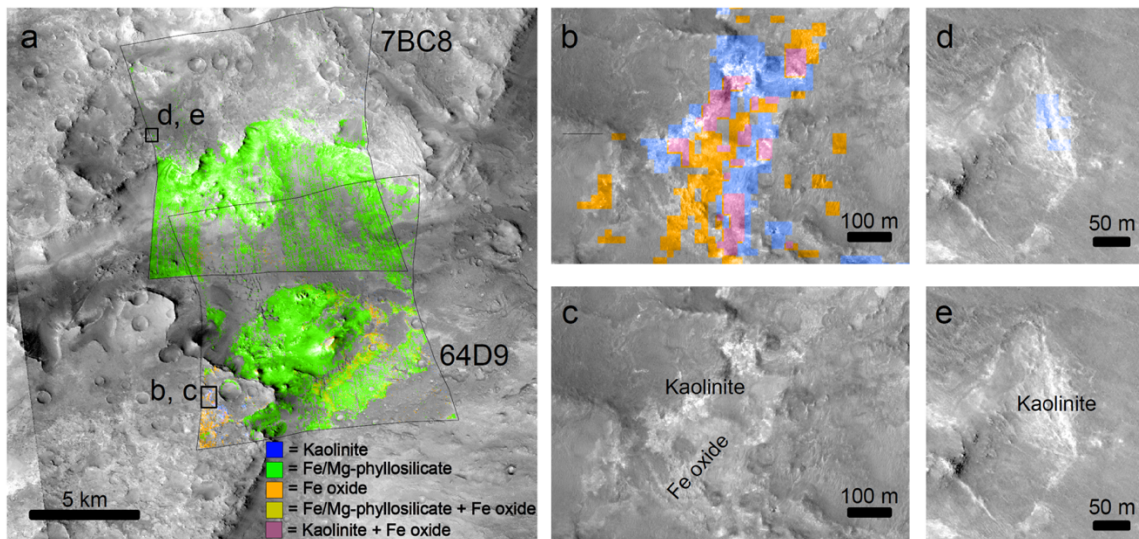


Figure 16: a) The full mineral map of image FRT000064D9 and FRT00007BC8 showing kaolinite, Fe/Mg-phylllosilicate, and Fe oxide along the edge of and within the main trough. b-c) Kaolinite and Fe oxide in 64D9 seemingly partially mixed at CRISM resolution, but the textures of these minerals in HiRISE 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).

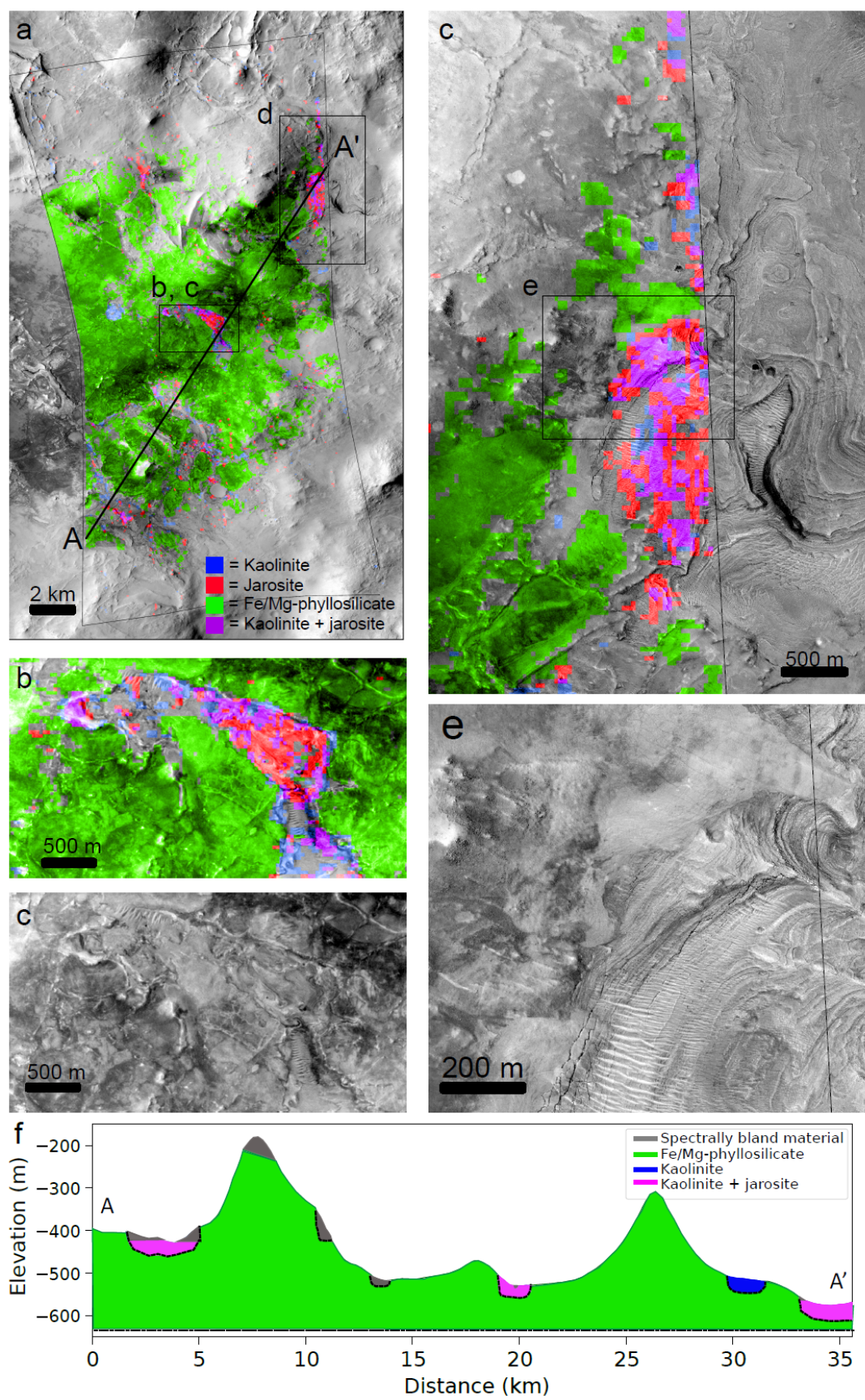


Figure 17: a) The full mineral map of the image AB0A showing Al-phyllosilicate, Fe/Mg-phyllosilicate, and jarosite fill in an impact crater adjacent to the north of the Nili Fossae troughs. The Fe/Mg-phyllosilicate corresponds to a rough, knobby unit that lacks visible layering, while jarosite and kaolinite 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.

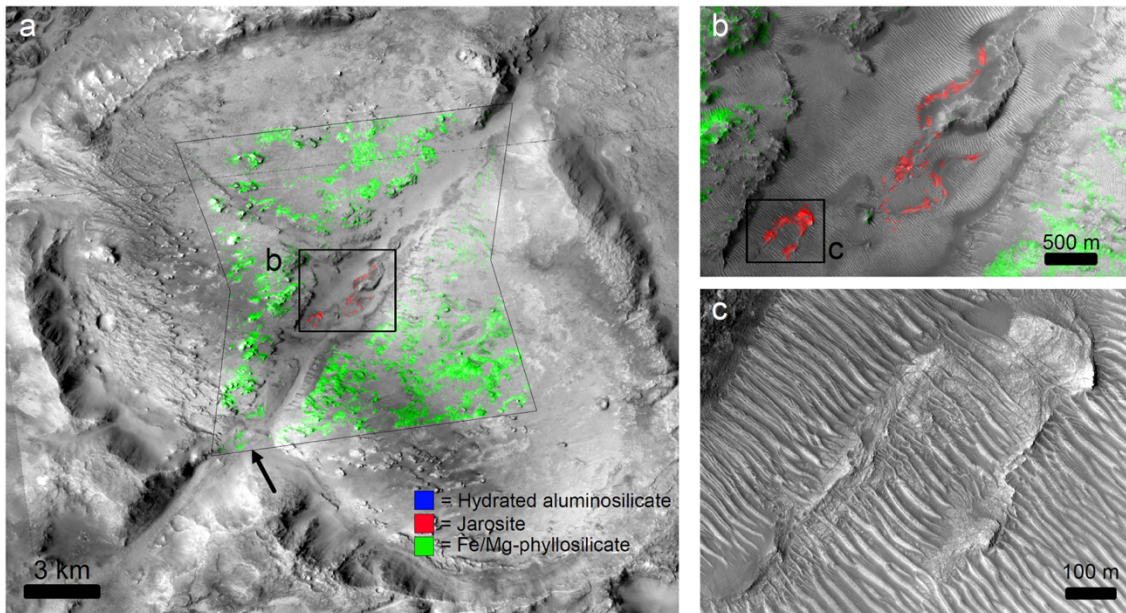


Figure 18: a) The full mineral map of the image FRT00003584 showing Fe/Mg-phylllosilicate on the floor of an impact crater bisected and deformed by a fracture and jarosite in the fill material. The arrow indicates a small amount of hydrated aluminosilicate type 2 in the fill material as well. b) The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

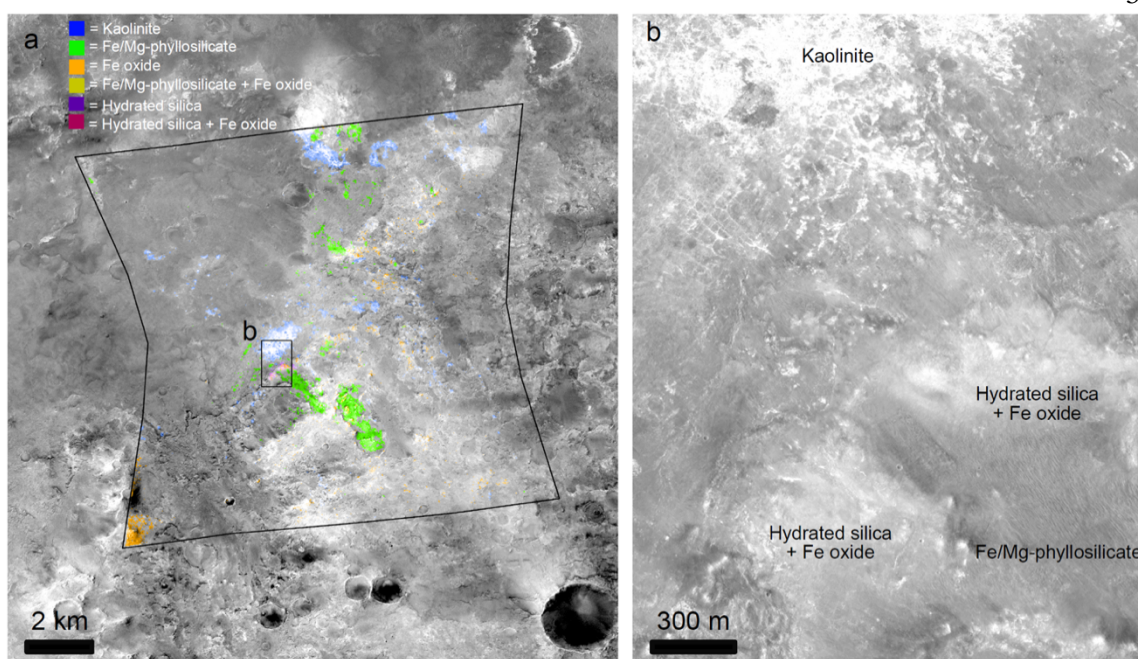


Figure 19: a) The full mineral map of the image FRT0000ABCB showing kaolinite, Fe/Mg-phylllosilicate, Fe oxide, and a small amount of hydrated silica in the large eroded topographic low to the west of the fossae. b) The textures and stratigraphic relationships of these minerals in HiRISE image PSP_001754_2020. 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-phylosilicate or Fe oxides mixed with the kaolinite. The formation of Fe/Mg-phylosilicate is thermodynamically favored over the formation of Al-phylosilicate 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-phylosilicate 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-phylosilicates 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-phyllsilicates, 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-phyllsilicate. 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-phyllsilicates. 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-phyllsilicate 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 phyllsilicates

In Nili Fossae, we do not find jarosite mixed nor associated with Fe/Mg-phyllsilicate. 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-phyllsilicate suggests that the water was not acidic, and there was a lack of sufficient S locally available from other sources like the Fe/Mg-phyllsilicate 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, SO₄ 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 indeterminant 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-phylllosilicate 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.

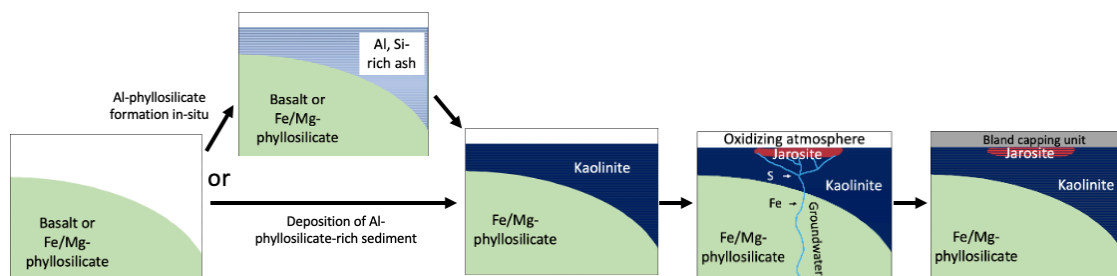


Figure 20: Proposed geologic history for the formation of Al-phyllsilicate in Nili Fossae. We propose that Al/Si-rich ash or Al-phyllsilicate-rich sediment was deposited on top of either basalt or Fe/Mg-phyllsilicate. Phyllosilicate formation occurred either pre-depositionally or in situ from the second 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-phyllosilicate 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-phyllosilicate consistently overlying Fe/Mg-phyllosilicate 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-phyllsilicate 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-phyllsilicate-bearing unit is draped over the underlying Fe/Mg-phyllsilicate (Wray et al., 2008). This apparent draping and the 10s of m thickness of these units has been interpreted to indicate Al-phyllsilicate 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-phyllsilicate 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 phyllsilicates 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-phyllosilicates 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-phyllosilicate deposits including kaolinite, montmorillonite, and aluminous nontronite have been detected overlying Fe/Mg-phyllosilicates 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-phyllosilicate 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-phyllosilicate and diminishing thickness of the unit away from the volcano Arsia Mons (Leask et al., 2024). These Al-phyllosilicates are found across the region but are concentrated in Columbus and Cross craters. Columbus Crater contains widespread Al-phyllosilicate, 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-phyllosilicate is exposed outside of Eridania, though crater ejecta indicates its presence at depth beneath the Al-phyllosilicate 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

CO₂ atmosphere likely produced widespread mildly acidic weathering conditions due to the formation of H₂CO₃ 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 CO₂ 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°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°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 (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-phylllosilicate (knobby, un laminated, 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-phylllosilicate 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-phylllosilicate 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>.

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Chapter 3

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

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Abstract

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

1 Introduction

Phyllsilicate (clay) minerals in Mars' Noachian terrains provide a mineralogic record of ancient water-rock interactions on the planet, recording ancient climate and

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

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

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

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

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

Additionally, much of the Al-phyllsilicate on Mars lacks associated Fe oxide, which is unexpected for basaltic alteration in an oxidizing environment (Nesbitt and Young, 1989; Gaudin et al., 2005; Greenberger et al., 2012). Fe oxide has been reported in association with Al-phyllsilicate in parts of Mawrth Vallis (Wray et al., 2008), but it has been searched for and not detected alongside Al-phyllsilicate in Valles Marineris (Le Deit et al., 2012) and Nili Fossae (Baker and Ehlmann, in review). In most Al-phyllsilicate bearing regions, however, the association of Al-phyllsilicate with Fe oxide has not yet been examined. This positive or negative detection of Fe oxide within the Al-phyllsilicate-bearing units is essential to help understand the pH and redox state of the alteration environment as well as the original availability of Fe in the system.

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

2 Previous Studies of Al-Phyllsilicate Regions

There have been numerous detailed local studies of the Al-phyllsilicate, and, where applicable, jarosite–alunite, for most of these regions of interest. These studies have revealed complexities that reflect local processes and chemistry. In some cases,

these studies contradict the observations that would be expected if Al-phyllsilicate formed from basalt as part of a pedogenic leaching sequence.

In Nili Fossae, there is widespread Al-phyllsilicate stratigraphically overlying Fe/Mg-phyllsilicate. Previous studies interpreted this stratigraphy to represent basaltic weathering sequences (Ehlmann et al., 2009). However, that analysis was before the detection of some jarosite deposits in the region (Ehlmann and Dundar, 2015), and without the most recent CRISM and HiRISE images. We therefore re-examined the Al-phyllsilicate in the context of its relationship to jarosite and with all available imagery. We found that the Al-phyllsilicate in this region is better explained by formation from an Al/Si-rich volcanoclastic sediment (e.g., ash) layer that was unconformably deposited on top of the Fe/Mg-phyllsilicate basaltic protolith. This is evidenced by the differences in texture between Al-phyllsilicate and Fe/Mg-phyllsilicate and several observed sharp contacts between them with no mixing at the CRISM resolution (18 m/pixel), and in some cases, there is spectrally bland material exposed between these phyllsilicates. Additionally, Al-phyllsilicate lacks the associated Fe oxide that would be expected if it formed from leaching of basalt under oxidizing conditions. Al-phyllsilicate is preferentially associated with topographic lows that form sedimentary basins, and it is often in m-scale layers within plateaus that also suggest its formation from sedimentary material. We detected sparse jarosite throughout the region, and it is associated with Al-phyllsilicate rather than Fe/Mg-phyllsilicate. This association of an Fe sulfate with only Al-phyllsilicate is unexpected if there was widespread acidic alteration in the region. Therefore, we argue that the requisite S to produce jarosite from Fe-bearing waters was likely locally-sourced from the Al-phyllsilicate ash protolith (Baker and Ehlmann, in review). No alunite has been reported in this region.

Analysis of Libya Montes is made difficult by the extensive dust cover, but studies have identified Al-phyllsilicate in several locations. Fe/Mg-phyllsilicate, thought to have formed from alteration of Noachian basalt, is widespread in this region (Bishop et al., 2013). Smaller deposits of Al-phyllsilicate have also been identified largely in eroded massif blocks or fluvial deposits, but they appear to be separate from the Fe/Mg-phyllsilicate-bearing units (Erkeling et al., 2012; Bishop et al., 2013). The

Al-phyllsilicate has been identified as beidellite ($((\text{Na}, \text{Ca}_{0.5})_{0.3} \text{Al}_2((\text{Si}, \text{Al})_4 \text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O})$), which often forms at higher temperatures than other Al-phyllsilicates like montmorillonite or kaolinite. Therefore, the beidellite may represent local hydrothermal conditions or burial diagenesis (Bishop et al., 2013). No jarosite or alunite has been reported in this region, and Fe oxide distribution has not been examined

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

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

Outside of Eridania Basin, thick (60–150 m) Al-phyllsilicates are found across the region, largely in impact craters (Wray et al., 2011; Ehlmann et al., 2016; Leask et al., 2024). Fe/Mg-phyllsilicates are found in crater ejecta, indicating its presence at depth

but with limited exposures at the surface (Leask et al., 2024). The Al-phyllsilicate, largely kaolinite with some montmorillonite, demonstrates increasing thickness of the unit towards the volcano Arsia Mons and often has m-scale layers. Because of this, it has been interpreted to have formed from alteration of a volcanic ash deposit emplaced unconformably over the Fe/Mg-phyllsilicate protolith (Leask et al., 2024), similar to our conclusion for Al-phyllsilicate formation in Nili Fossae (Baker and Ehlmann, in review). Alunite is found within some of the Al-phyllsilicate across the region (Swayze et al., 2008; Ehlmann et al., 2016; Leask et al., 2024). It has been interpreted to have formed from the upwelling of acidic groundwater, possibly acidified through interaction with S-enriched magma (Ehlmann et al., 2016; Leask et al., 2024). Fe oxide has not been reported in this region.

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

and/or hydrated silica with jarosite or Fe/Mg-phylllosilicate, gypsum or an alternative sulfate, or acid-altered Al/Fe-phylllosilicate (e.g. Tosca, 2008; Roach et al., 2010). Alunite has been detected in two locations in Valles Marineris alongside hydrated silica and possible Al-phylllosilicate (Viviano et al., 2013). Abundant Fe oxide has been detected within the Valles Marineris chasms in association with sulfate (Le Deit et al., 2008; Roach et al., 2010), though its association with Al-phylllosilicate or the doublet material has not been examined.

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

through alteration of a pyrite-bearing layer (Farrand et al., 2009). Small amounts of alunite have also been detected mixed with Al-phyllsilicate, sometimes in association with jarosite as well (Miura et al., 2019; Poulet et al., 2020; Bishop et al., 2023). Fe oxides including possible hematite and goethite have been reported to be mixed with some of the Al-phyllsilicate throughout this region (Wray et al., 2008) and to be mixed with jarosite (Farrand et al., 2009).

These reviews of the primary Al-phyllsilicate-bearing regions demonstrate that there is substantial complexity and diversity in their formation processes on a regional scale. Studies that address these Al-phyllsilicate-bearing regions on a global scale often treat all the Al-phyllsilicate as indicative of extensive weathering in a pedogenic leaching sequences despite the variation in the mineralogy and stratigraphic configuration of Al-phyllsilicate and accompanying phases across these regions (e.g. Carter et al., 2015; Moore et al., 2025; Klidas et al., 2025).

3 Methods

3.1 Data processing

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

To reduce column-specific noise in the spectral data, we calculated the ratio of every spectrum to the representative bland spectra in its image column. To identify these bland spectra, we used the method described in Baker and Ehlmann (in review), which was

originally based on a method developed by Pan et al. (2017). In this method, the bland spectra in each column prior to map-projection were defined as those that had values below the mean + 1.5 * the standard deviation value in a column for these spectral parameters produced by Viviano et al. (2014): BD530_2, BD860_2, BD1400, OLINDEX3, LCPINDEX2, HCPINDEX2, BD1750_2, BD1900_2, BD2190, BD2250, BD2265, BD2290, and BD2355. For this study, we added an additional criterion that the value of BD2290 for a spectrum must be < 0.003 for that spectrum to be included in this bland pool. Without this additional criterion, Fe/Mg-phylllosilicate-bearing spectra were occasionally included in the bland pool if a column had a sufficiently high areal coverage of Fe/Mg-phylllosilicate (Baker and Ehlmann, in review), and this step worked to reduce this erroneous inclusion. Of these bland spectra, we then took the mean of those that had the 9 smallest integrated areas in the wavelength range 1869–2417 nm to be the denominator spectra for column ratioing. We then applied a Savitzky-Golay filter with a bin width of five channels and a polynomial order of two to each ratioed spectrum for additional denoising.

3.2 Mineral identification

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

mineral of interest if the depth of the fit Gaussian exceeded 3x the standard deviation of that column's bland spectrum in that wavelength range.

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

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

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

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

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

To identify alunite, which is often mixed with Al-phyllsilicate and so can be difficult to isolate, we combined the above methods with examination of the wavelength of the minimum of the absorption feature and other diagnostic absorptions. Alunite has diagnostic absorptions at 1750 nm as well as 2165 nm. For each image that was found to contain a phase absorbing near 2200 nm, we examined by hand the respective map of the BD1750_2 parameter made by Viviano et al. (2014) to identify pixels with absorptions at this position. We also generated maps in which we plotted the wavelength position of the minimum of the ~ 2200 nm absorption for all pixels identified as containing an absorption near this location. From these maps, we were able to identify pixels with absorption minima short what would be expected for Al-phyllsilicate alone. Spectra that contained these shorter ~ 2200 nm absorptions and an absorption at 1750 nm were identified as containing alunite.

Table 1

Relevant Minerals and Their Absorptions

Mineral group	Mineral name	Formula	Diagnostic absorption(s) (nm) used here	Cause of absorption
Al-phyllsilicate	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	2165 and 2205 doublet	Al-OH vibrational
	Montmorillonite	$(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2215	Al-OH vibrational
Fe/Mg-phyllsilicate	Nontronite	$\text{Na}_{0.3}\text{Fe}_2((\text{Si,Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2285	Fe-OH vibrational
	Saponite	$\text{Ca}_{0.25}(\text{Mg,Fe})_3((\text{Si,Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$	2315	Mg-OH vibrational

Sulfate group	Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	2265	Fe-OH vibrational
	Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$	2165	Al-OH vibrational
Hydrated silica	Opal	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	2210–2245 (broad)	Si-OH vibrational
Fe oxide/hydroxide	Hematite	Fe_2O_3	540	Fe electronic charge transfer
	Goethite	$\text{FeO}(\text{OH})$	490	Fe electronic charge transfer
	Ferrihydrite	$\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$	525	Fe electronic charge transfer
	Lepidocrocite	$\text{FeO}(\text{OH})$	490	Fe electronic charge transfer

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

3.3 Examining stratigraphic relationships and geologic context

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

Table 2

Mineral Identification Process and Criteria

Target mineral(s)	Number of Gaussian curves fit	Free variables	Pre-set variables	Wavelength range fit	Limits on center position	Other criteria
Al- phyllosilicate, hydrated silica, alunite	1	Depth, center wavelength, width	N/A	2112.87 nm – 2331.02 nm	2159.83 nm– 2279.98nm	BD2190 or BD2250 > 0.006 or BD2205(ratioed)>0.0035 or BD2212(ratioed)>0.0028 and LCPINDEX2 < 0.027 Once fit, exclude pixels with centers > 2250.02 nm
Fe/Mg- phyllosilicate	1	Depth, center wavelength, width	N/A	2245.04 nm– 2390.58 nm	2,304.15 nm – 2,400.38 nm	BD2290 > 0.004 or BD2311(ratioed) > 0.002
Jarosite	2	Depth, width	Center wavelengths	2112.87 nm –2331.02 nm	Fixed at 2265.01 nm and 2205.07 nm	BD2265>0.003 and R2284.72>R2264.88
Fe oxide	1	Depth, center wavelength, width	N/A	442 nm – 631 nm	400 nm – 600 nm	BD530 > 0.16, fit Gaussian depth > BD625

Details of the Gaussian fitting algorithm applied to identify each group of minerals, limits applied to free variables, and other criteria a spectrum had to meet to be considered to contain the relevant target mineral.

4 Results

4.1 Global distribution of Al-phyllosilicate and accompanying phases

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

sparse, scattered Fe/Mg-phyllosilicate is exposed, but it likely exists at depth beneath the Al-phyllosilicate.

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

The distribution of Fe oxide in association with Al-phyllosilicate is uneven across the globe. In Nili Fossae, Libya Montes, and eastern Terra Sirenum, we do not detect Fe oxide mixed with Al-phyllosilicate. We frequently see a mixture of Fe oxide with at least some Al-phyllosilicate exposures in Hellas Planitia, Eridania Basin, and Mawrth Vallis. In Valles Marineris, much of the Al-phyllosilicate that is exposed at depth in the chasms is associated with Fe oxide. In this region, the Fe oxide is also strongly correlated with jarosite.

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

4.2 Comparative spectral analysis of Al-phyllosilicate and accompanying phases

4.2.1 Al-phylosilicate mineralogy

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

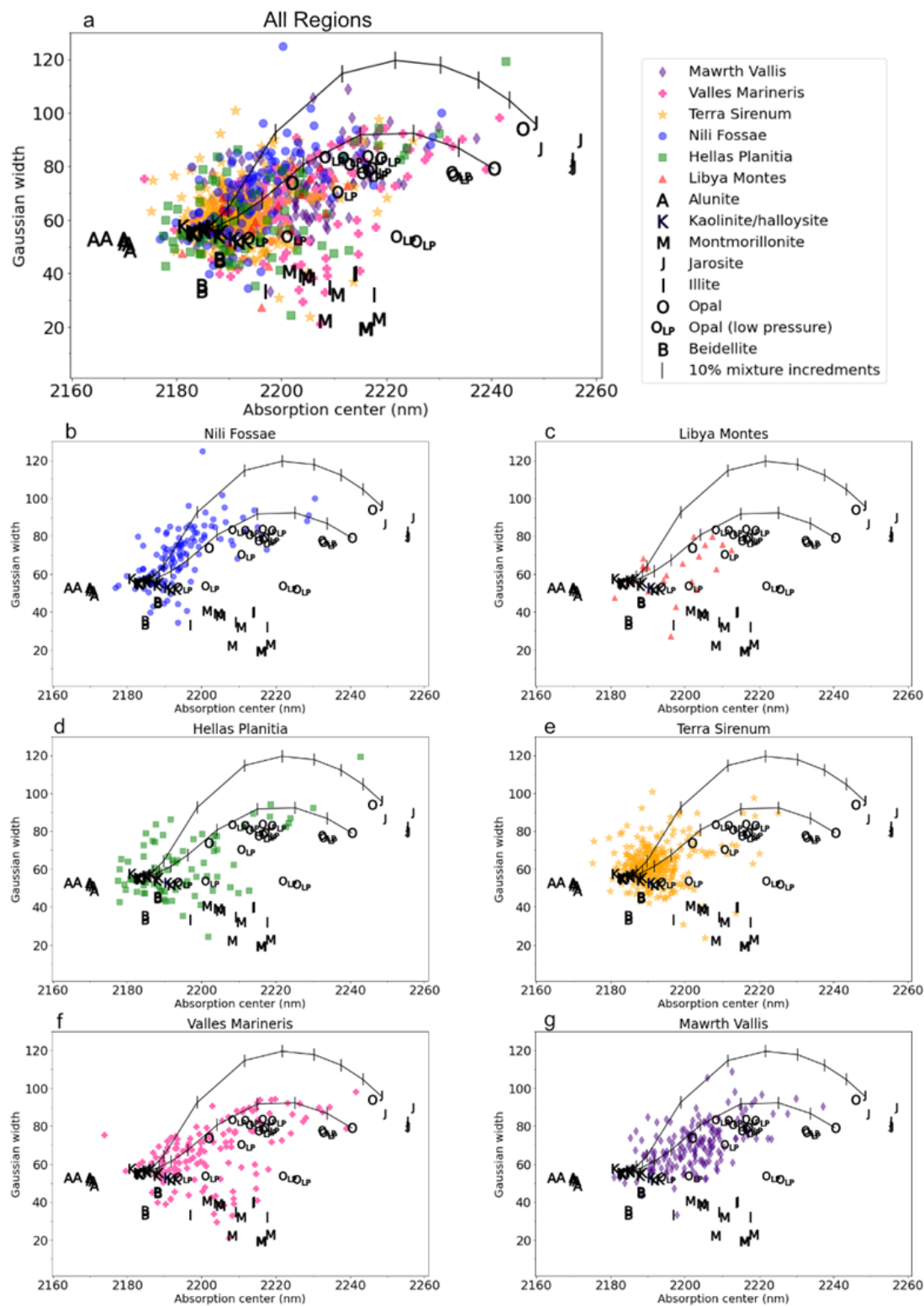


Figure 1: Scatterplots of the fit Gaussian width versus the fit Gaussian center position. Each point represents the fit to the mean spectrum of an ROI. Gaussian fits to laboratory spectra and two modeled linear mixtures are plotted for comparison. Laboratory spectra were taken from USGS and RELAB, and low pressure opal measurements were taken from Sun (2017). a) All Al-phyllsilicate ROIs we identified from every region. b-g) Scatterplots for each region shown in a plotted individually.

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

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

In Hellas Planitia (Figure 1d, Figure 2d), both kaolinite and montmorillonite appear to be common compositions for the Al-phyllsilicate, though montmorillonite is more prevalent. We also detect a small number of possible beidellite deposits, as well as an aluminosilicate that is wide and symmetric but absorbs at ~2180 nm, short of the other

aluminosilicates detected. The hydrated silica in this region is narrower than the opal detected in Nili Fossae.

Similar to Nili Fossae, we find that the Al-phylllosilicate in Terra Sirenum (Figure 1e, Figure 2e) is dominantly kaolinite, though it also contains a small number of montmorillonite detections. We also detect a wide aluminosilicate similar to that in Nili Fossae and Libya Montes, and we find hydrated silica. Like Nili Fossae, we identify jarosite as well as jarosite mixed with Al-phylllosilicate (likely kaolinite). We also detect alunite mixed with Al-phylllosilicate, as indicated by its broad absorption at ~2165 nm combined with an absorption at ~1750 nm not shown here.

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

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

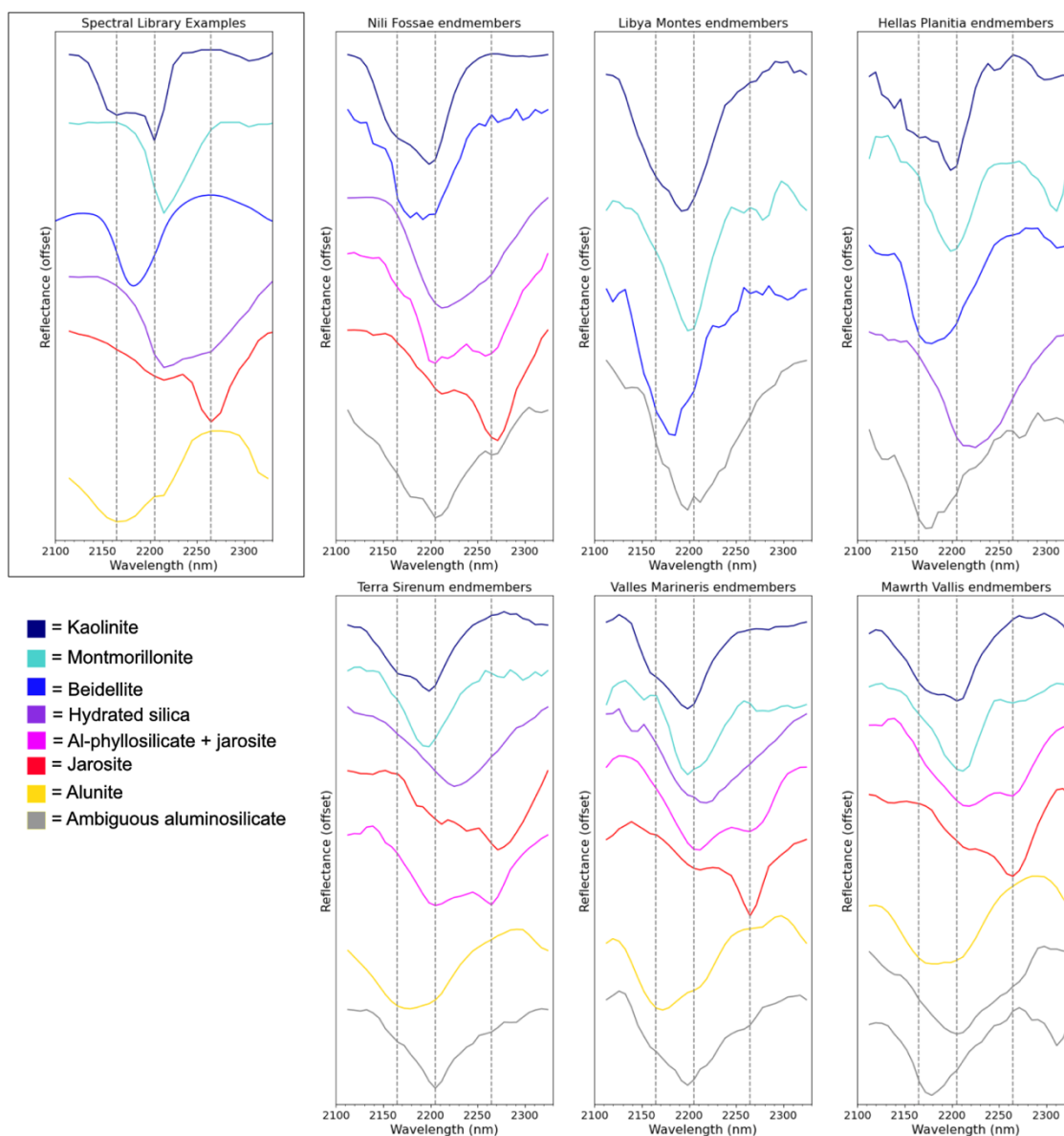


Figure 2: a) Endmember spectra of Al-phyllsilicate and associated minerals from laboratory spectral libraries and, b-g) manually selected from each region. All spectra were continuum-removed from 2100–2330 nm and normalized between 0–1 before being offset. Each CRISM endmember represents the mean spectrum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

4.2.2 Al-phyllsilicate + jarosite mixtures

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

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

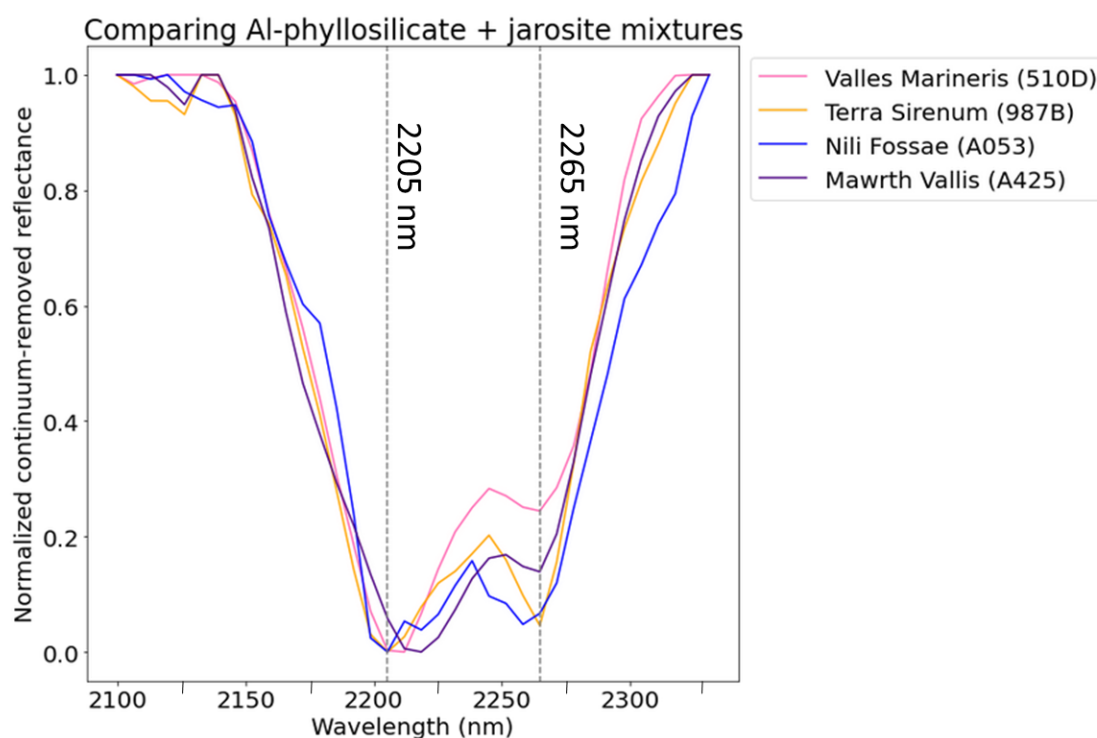


Figure 3: Example spectra of what we conclude is most likely mixed Al-phyllsilicate and jarosite in Valles Marineris, Terra Sirenum, Nili Fossae, and Mawrth Vallis. Each spectrum is the mean spectrum of an ROI taken from the listed image. Each spectrum was continuum-removed from 2100–2330 nm and normalized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

4.2.3. Fe oxide

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

examples lack similar laboratory spectra. We conclude that these phases are most likely a mixture of multiple Fe-bearing phases, and we refer to it generally as Fe oxide. We excluded false positive detections of Fe oxide that appear to be due to a spectral artifact created by direct illumination of topographic faces.

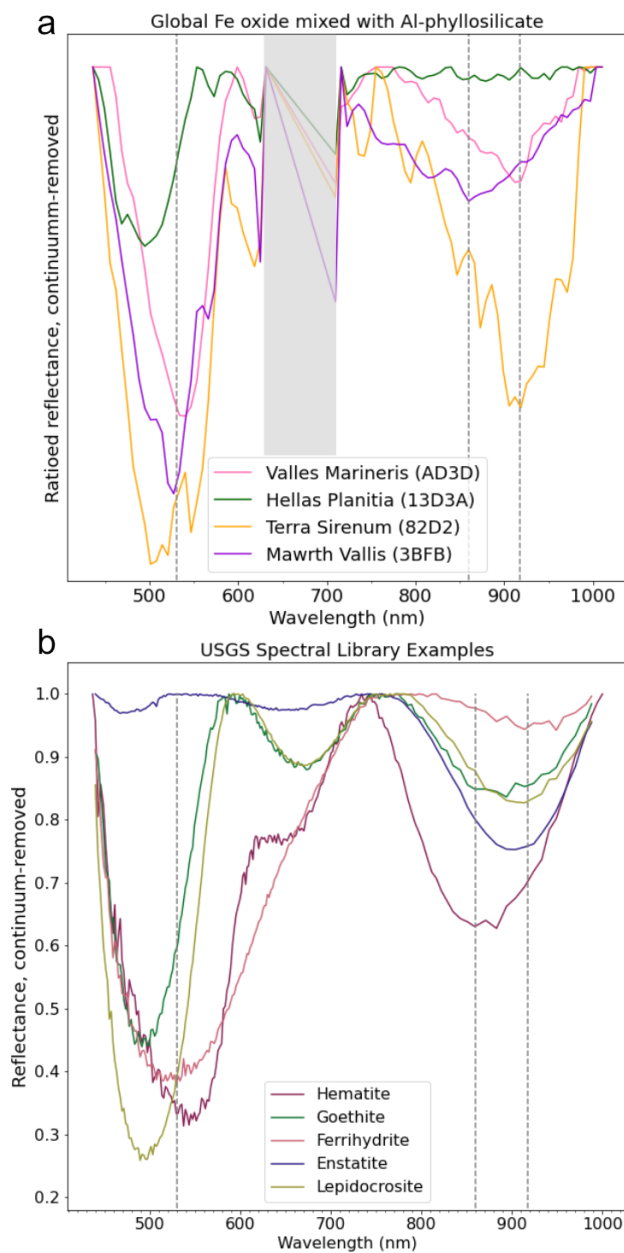


Figure 4: Representative examples of spectra of the minerals absorbing around 500 nm and/or 900 nm that are observed mixed with Al-phyllsilicate across Mars compared to laboratory samples. a) Short wavelength range continuum-removed mean spectra of all mixed Fe oxide and Al-phyllsilicate in the given image. The obscured area between 631 nm – 710 nm represents a CRISM filter break (Murchie et al., 2007). b) Continuum-removed spectra of Fe oxides and pyroxene taken in the laboratory from the USGS spectral library (Kokaly et al., 2017) for reference.

4.3 Stratigraphic association of Al-phyllsilicate and accompanying phases

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

4.3.1 Al-phyllsilicate formation from weathering sequences

4.3.1.1 Hellas Planitia

Consistent with prior findings (Carter et al., 2015), Al-phyllsilicate and Fe/Mg-phyllsilicate are abundant in the plains north of Hellas Planitia. These plains are largely

Noachian sedimentary plains, as indicated by their fine layering (Salese et al., 2016). We detect Al-phyllsilicate in 27 images, largely in the sedimentary intercrater plains, though some deposits are in crater rims or sedimentary crater infill (Figure 5).

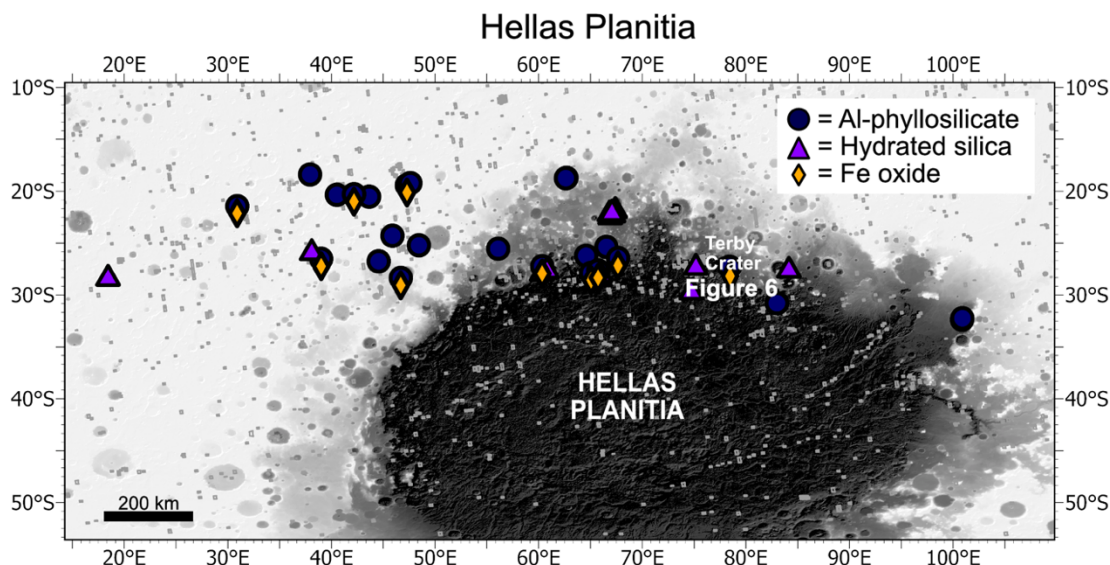


Figure 5: Distribution of detections of Al-phyllsilicate, hydrated silica, and Fe oxide (where it is detected in Al-phyllsilicate-bearing images) in Hellas Planitia within CRISM MTRDR images (footprints in gray). The location of subsequent Figure 6 is labeled. The basemap is the MOLA interpolated DEM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

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

imagery indicates that there appears to be a gradational transition from one mineral to the other.

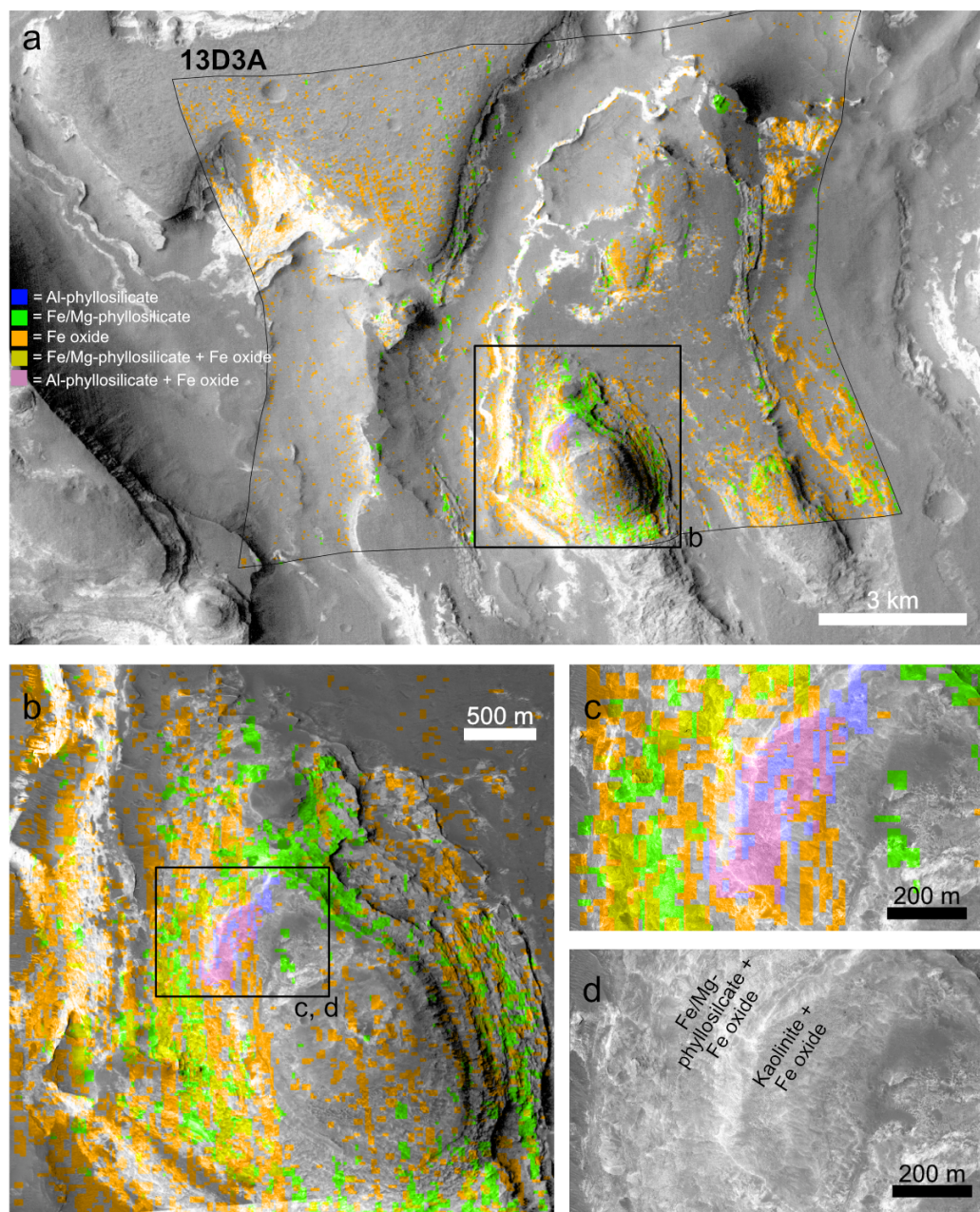


Figure 6: a) The full mineral map of image FRT00013D3A showing kaolinite, Fe/Mg-phylosilicate, and Fe oxide within layered deposits on the northern edge of Hellas Planitia. b) The central mound of this deposit showing Al-phylosilicate stratigraphically

overlying Fe/Mg-phyllosilicate, both mixed with Fe oxide. c, d) A close-up of the phyllosilicate stratigraphy showing that both phyllosilicates have similar fractured textures with a conformable, gradational transition between them.

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

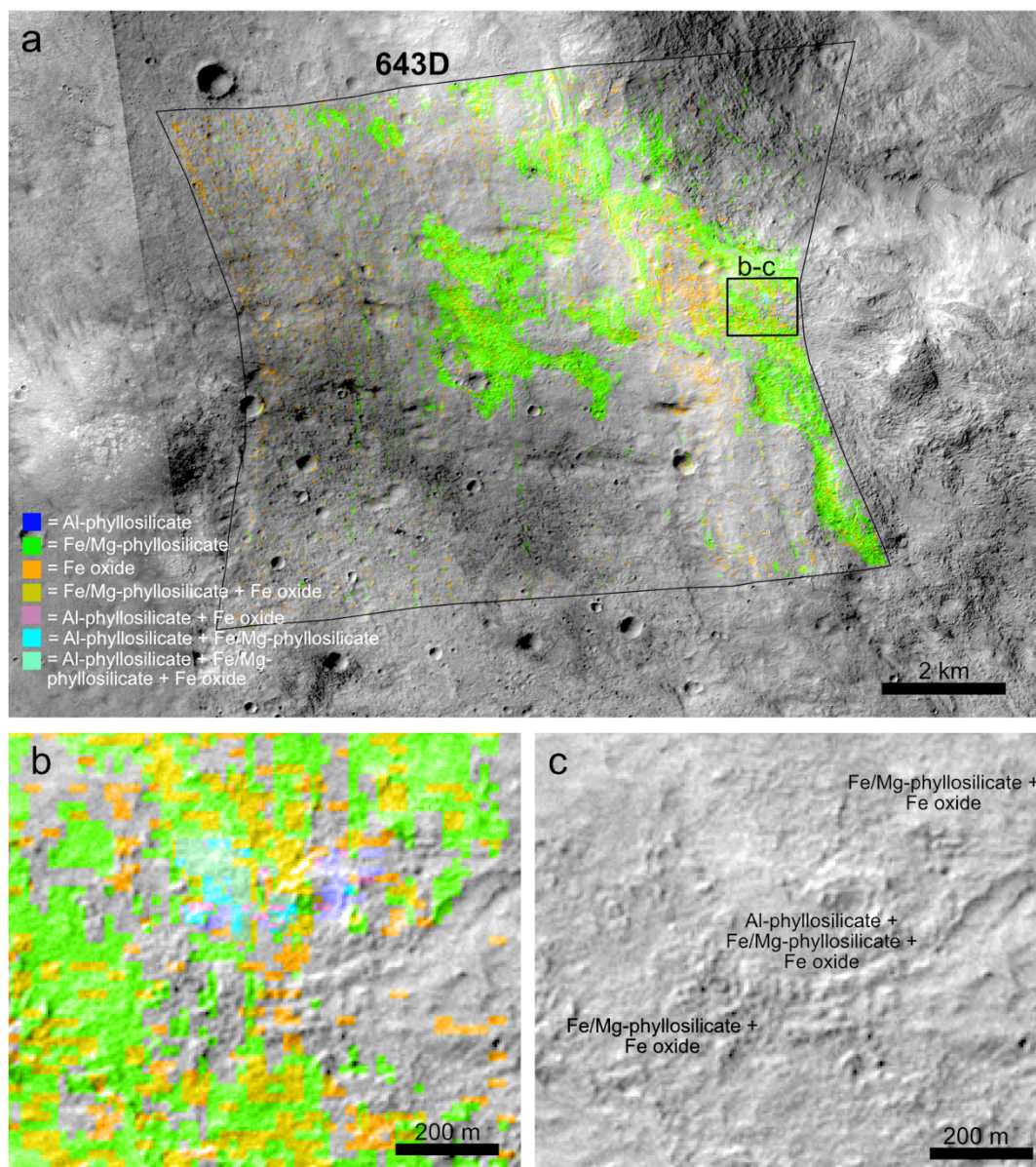


Figure 7: a) The full mineral map of image FRT000643D showing kaolinite, Fe/Mg-phyllsilicate, and Fe oxide within the sedimentary intercrater plains on the northern edge of Hellas Planitia. b, c) Close-up example of the Al-phyllsilicate, which is largely mixed with Fe/Mg-phyllsilicate and Fe oxide. At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

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

detect Fe oxide mixed with both Fe/Mg-phyllosilicate and Al-phyllosilicate in 13D3A (Figure 6c) and 643D (Figure 7b). Neither jarosite nor alunite were detected in this region.

4.3.1.2 Eridania Basin, western Terra Sirenum

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

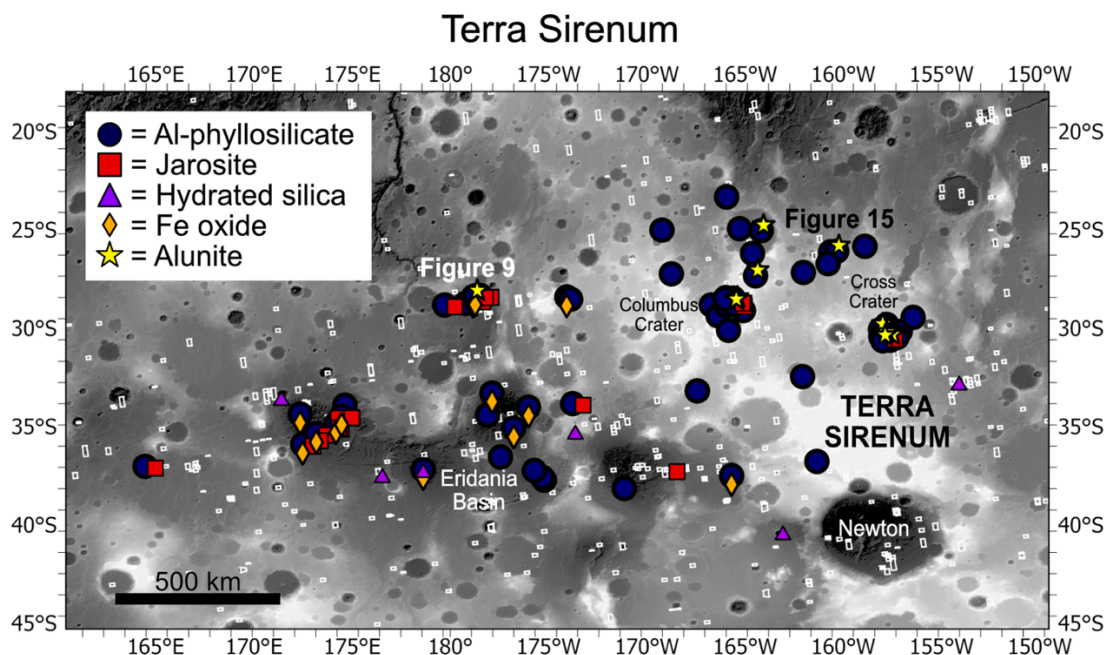


Figure 8: Distribution of detections of Al-phyllsilicate, hydrated silica, and Fe oxide (where it is detected in Al-phyllsilicate-bearing images) in Terra Sirenum within CRISM MTRDR images (footprints in gray). The locations of subsequent figures 9 and 15 are labeled. The basemap is the MOLA interpolated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

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

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

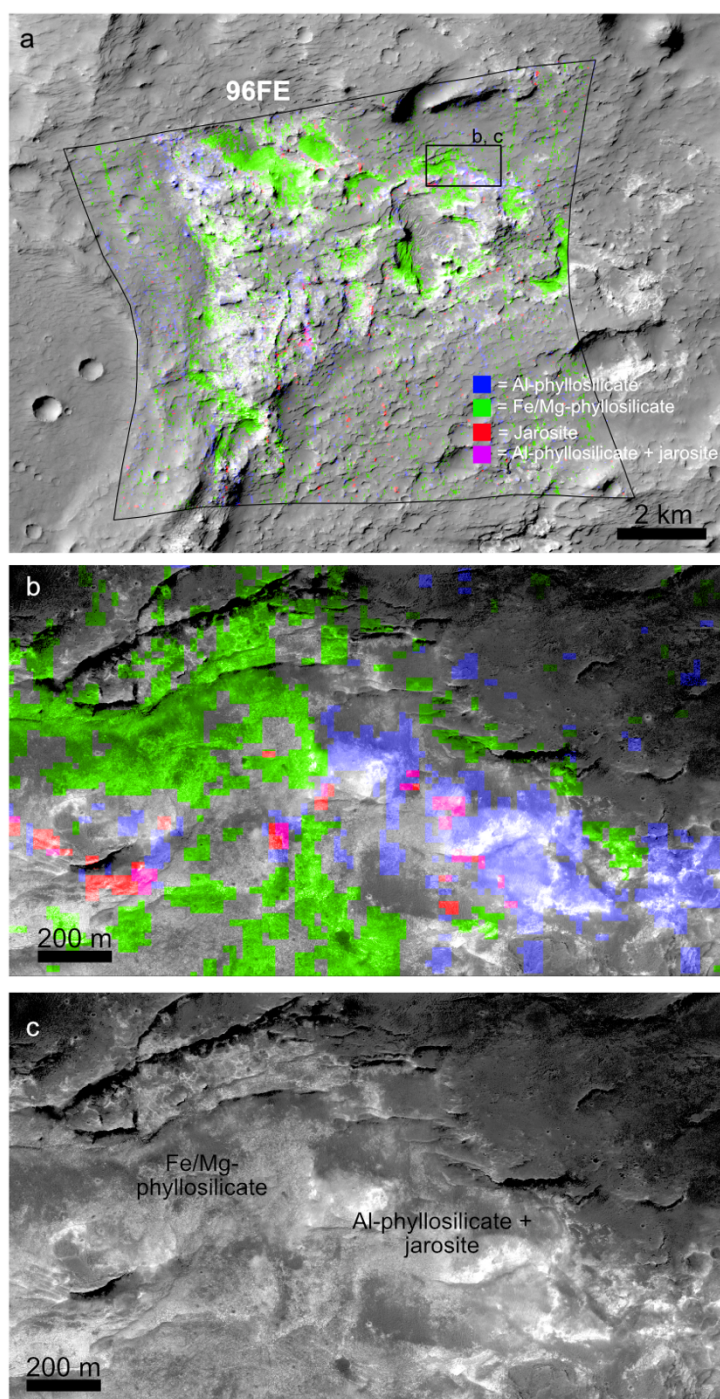


Figure 9: a) The full mineral map of the image FRT000096FE showing Al-phyllsilicate, Fe/Mg-phyllsilicate, and jarosite in light-toned deposits within Eridania Basin. b, c) A close-up of the phyllosilicate units. Al-phyllsilicate is mixed with sparse jarosite. Both Al-phyllsilicate and Fe/Mg-phyllsilicate have similar textures with m-scale polygonal

fractures, and there is no sharp unconformable contact between them. Instead, there appears to be a conformable, gradational contact.

4.3.2 Al-phyllsilicate formation from volcanoclastic alteration

4.3.2.1 Nili Fossae

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

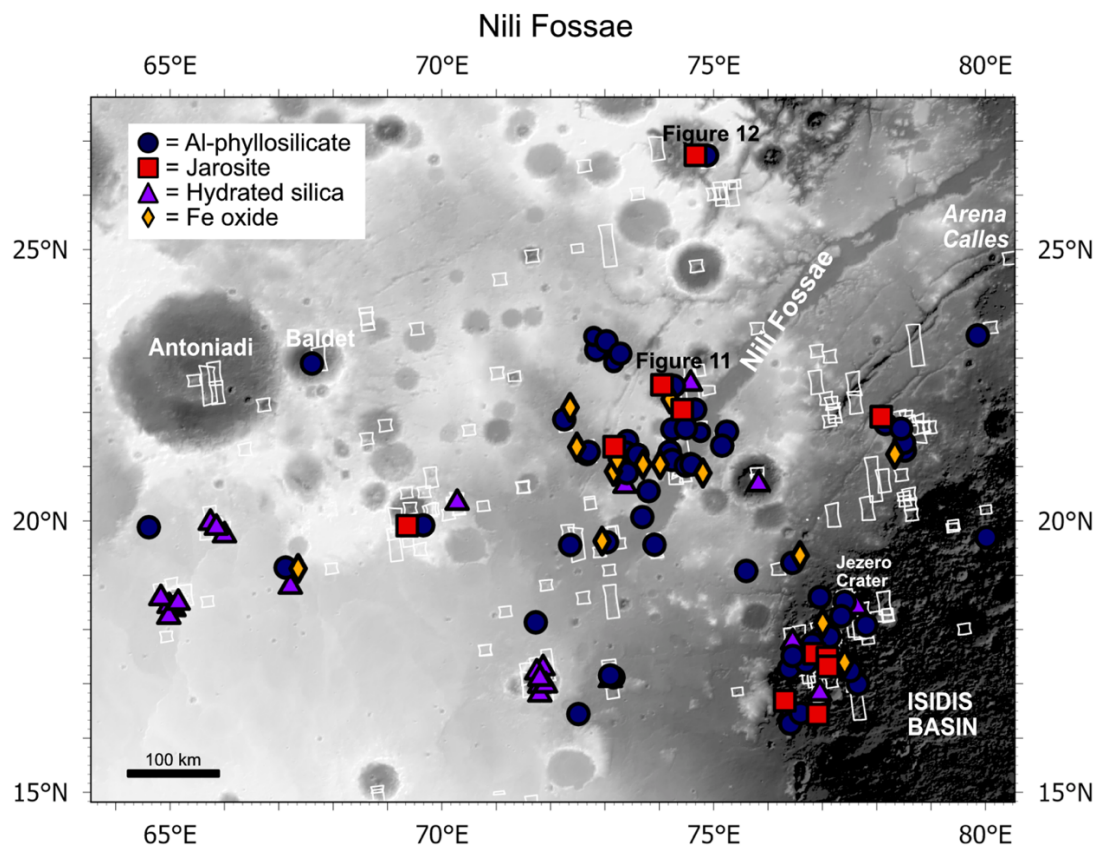


Figure 10: Distribution of detections of Al-phylllosilicate, jarosite, hydrated silica, and Fe oxide (where it is detected in Al-phylllosilicate-bearing images) in Nili Fossae within CRISM MTRDR images (footprints in white). The locations of subsequent figures 11 and 12 are labeled. The basemap is the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

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

Fe/Mg-phylllosilicate units mostly appear knobby, rough, and unlaminated, though some patches have similar polygonal fractures to the kaolinite.

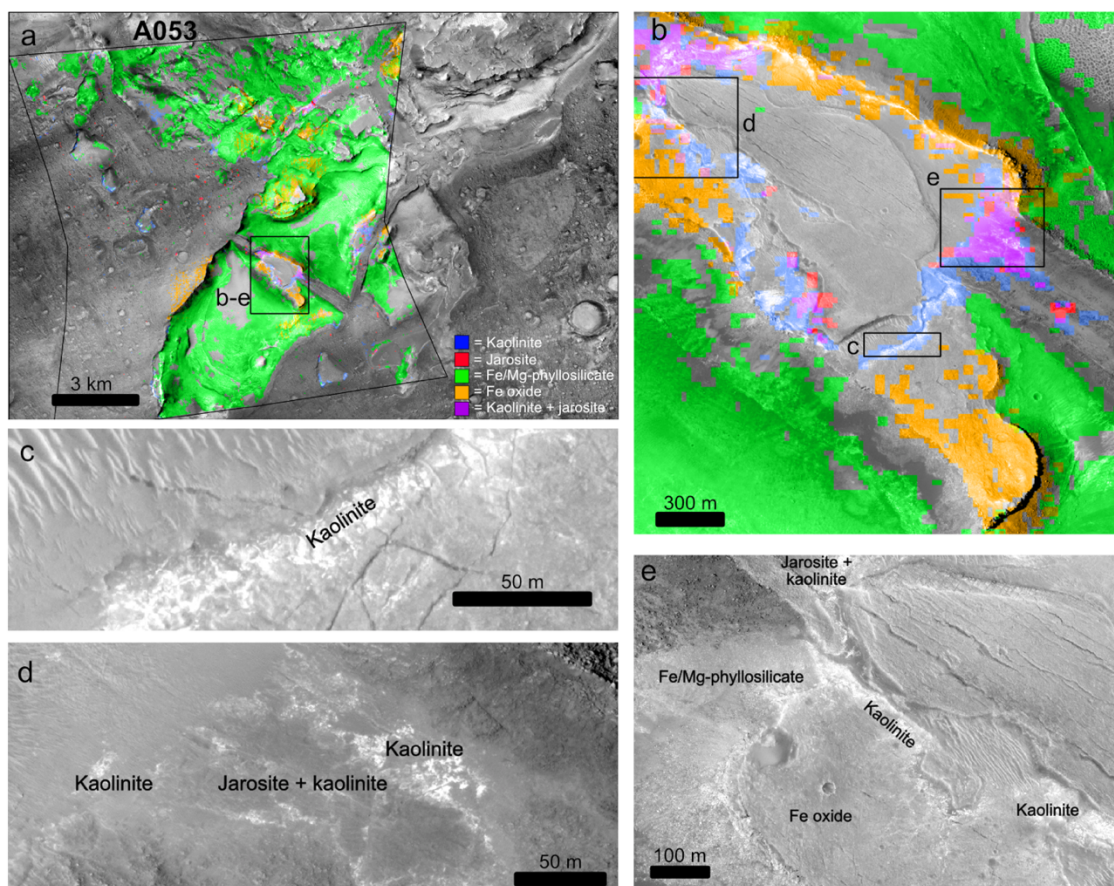


Figure 11: a) The full mineral map of FRT0000A053 showing Al-phylllosilicate, Fe/Mg-phylllosilicate, jarosite, and Fe oxide in crater sedimentary fill. A large aeolian-carved pit exposes several hundred m of Fe/Mg-phylllosilicate, with kaolinite and jarosite around the edges of two remnant plateaus.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

We identify five deposits of jarosite in Nili Fossae, all closely associated with Al-phylllosilicate. In some cases, such as in AB0A, the jarosite appears intimately mixed throughout the kaolinite (Figure 12b). In others, the strongest jarosite signal aligns with discrete darker-toned patches in contact with and mixed with lighter-toned kaolinite (e.g. in A053, Figure 11d). Fe oxide sometimes occurs within the same images as Al-phylllosilicate in this region (Figure 10), but it is not found to be mixed with the Al-phylllosilicate and is instead observed on its own or mixed with Fe/Mg-phylllosilicate (Figure 11a). In A053, where Fe oxide occurs adjacent to kaolinite, it is not mixed with it but instead corresponds to a texturally distinct unit stratigraphically between the Al-phylllosilicate and the underlying Fe/Mg-phylllosilicate (Figure 11e).

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

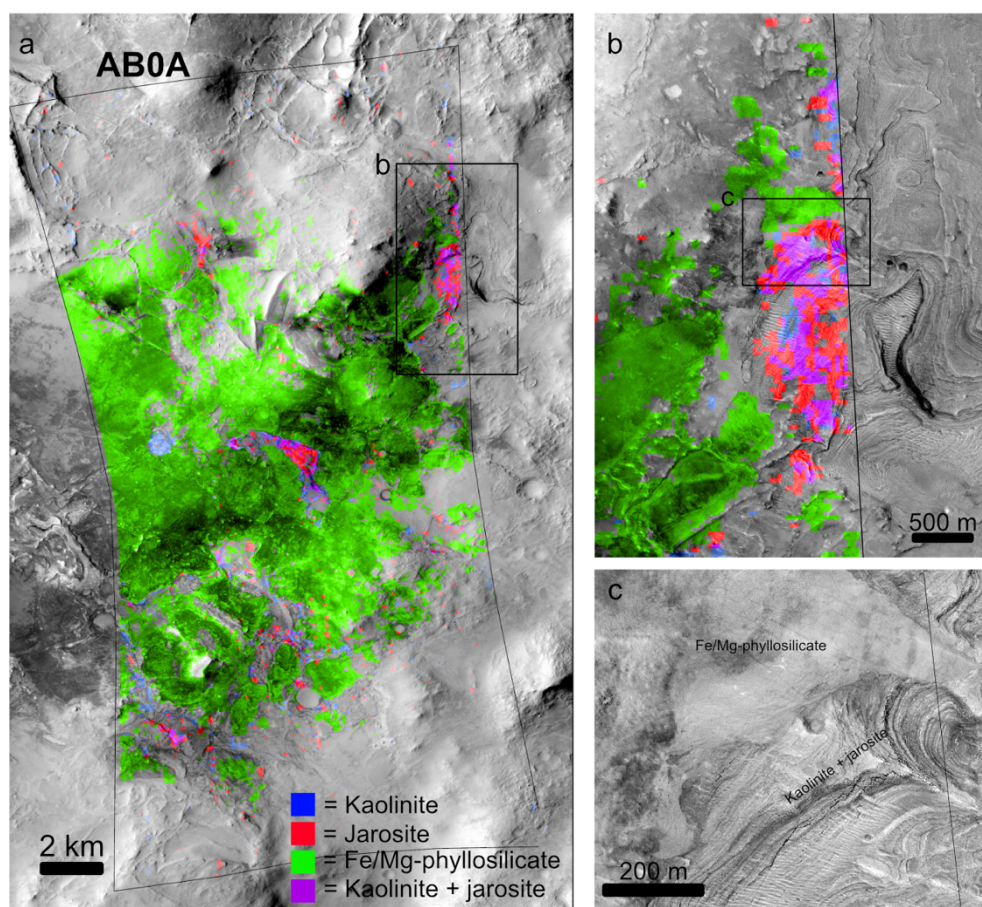


Figure 12: a) The full mineral map of HRL0000AB0A showing Al-phyllsilicate, Fe/Mg-phyllsilicate, and jarosite in crater sedimentary fill. b) The alteration mineralogy stratigraphy exposed by a canyon carved through this fill. The Fe/Mg-phyllsilicate unit is rough, knobby, and lacks visible layering.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

4.3.2.2 Libya Montes

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

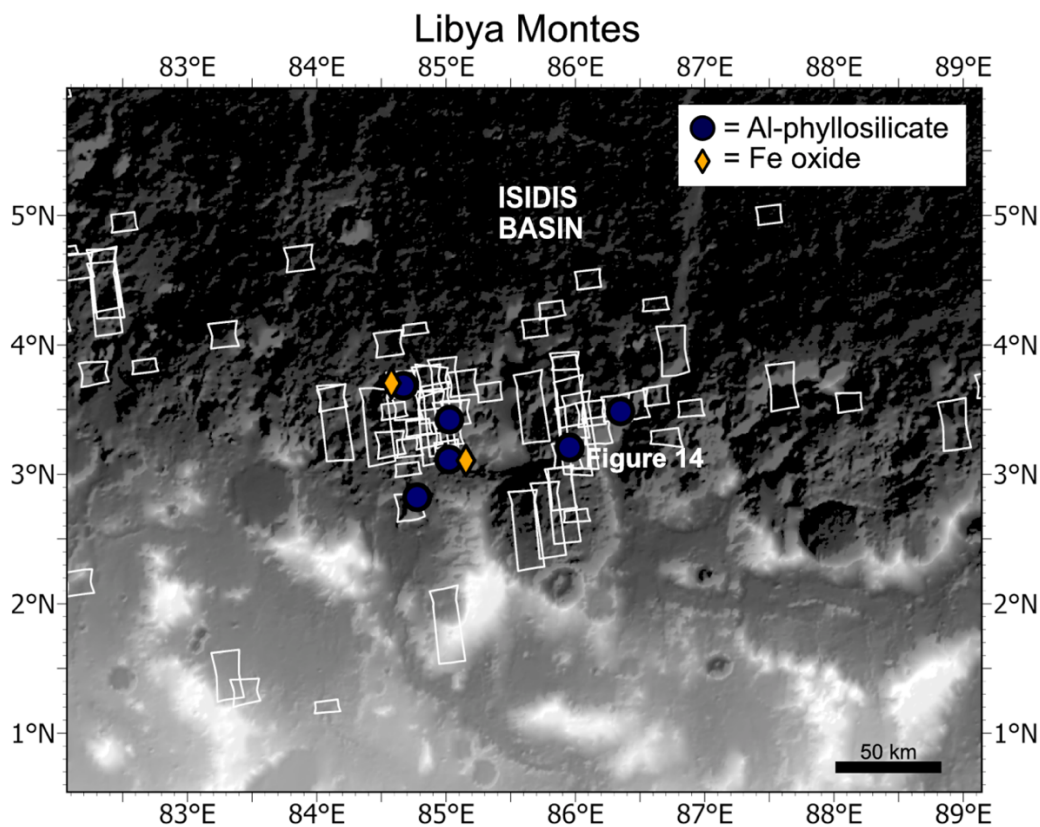


Figure 13: Distribution of detections of Al-phyllsilicate and Fe oxide (where it is detected in Al-phyllsilicate-bearing images) in Libya Montes within CRISM MTRDR images (footprints in white). The location of subsequent figure 14 is labeled. The basemap is the MOLA interpolated DEM (USGS).

We observe Al-phyllsilicate in two primary contexts: eroding out of blocks exposed in crater floors and a channel wall, and in layered sedimentary deposits. These blocks have been previously interpreted to be Noachian massifs that likely pre-date and were disrupted by the Isidis impact (Bishop et al., 2013), so it is challenging to interpret the original phyllsilicate stratigraphy. However, there is no observable mixing of Al-phyllsilicate and Fe/Mg-phyllsilicate, and they appear to occur in distinct geologic units. In present-day Libya Montes, these blocks are exposed in crater and channel walls and floors and so have likely been even further disrupted. We observe similar these Al-phyllsilicate-bearing blocks in four of the seven Al-phyllsilicate-bearing images in this region.

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

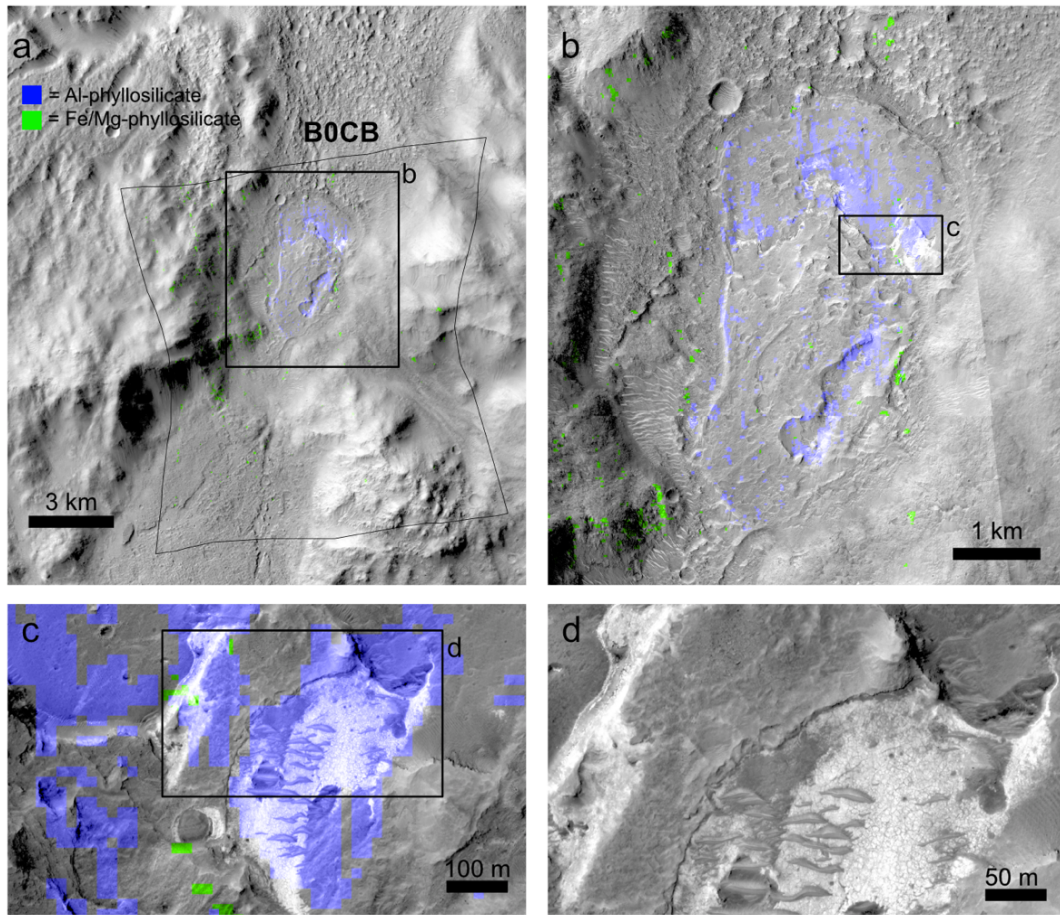


Figure 14: a) The full mineral map of the image FRT000B0CB showing Al-phyllsilicate and Fe/Mg-phyllsilicate in a layered deposit in the neck of an impact crater outflow channel. b) Al-phyllsilicate on the edges and within exposed layers of this deposit. c) Close-up example showing the association of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

4.3.2.3 Terra Sirenum

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

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

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

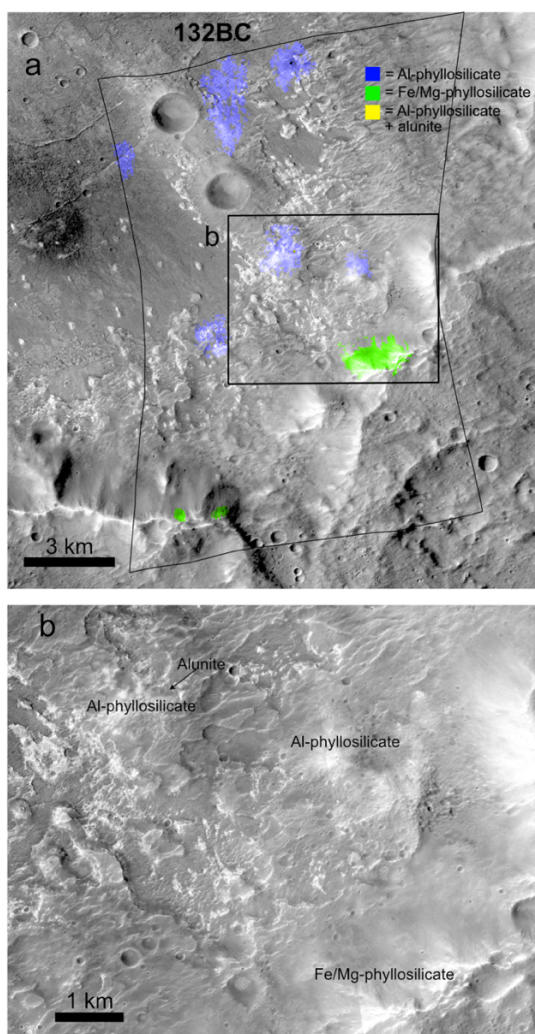


Figure 15: a) The full mineral map of the image HRL000132BC showing Al-phyllsilicate, Fe/Mg-phyllsilicate and a small deposit of alunitite within infill material in an impact crater. b) Close-up example showing the Fe/Mg-phyllsilicate exposed in the crater wall, while Al-phyllsilicate and alunitite are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

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

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

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

4.3.2.4 Valles Marineris

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

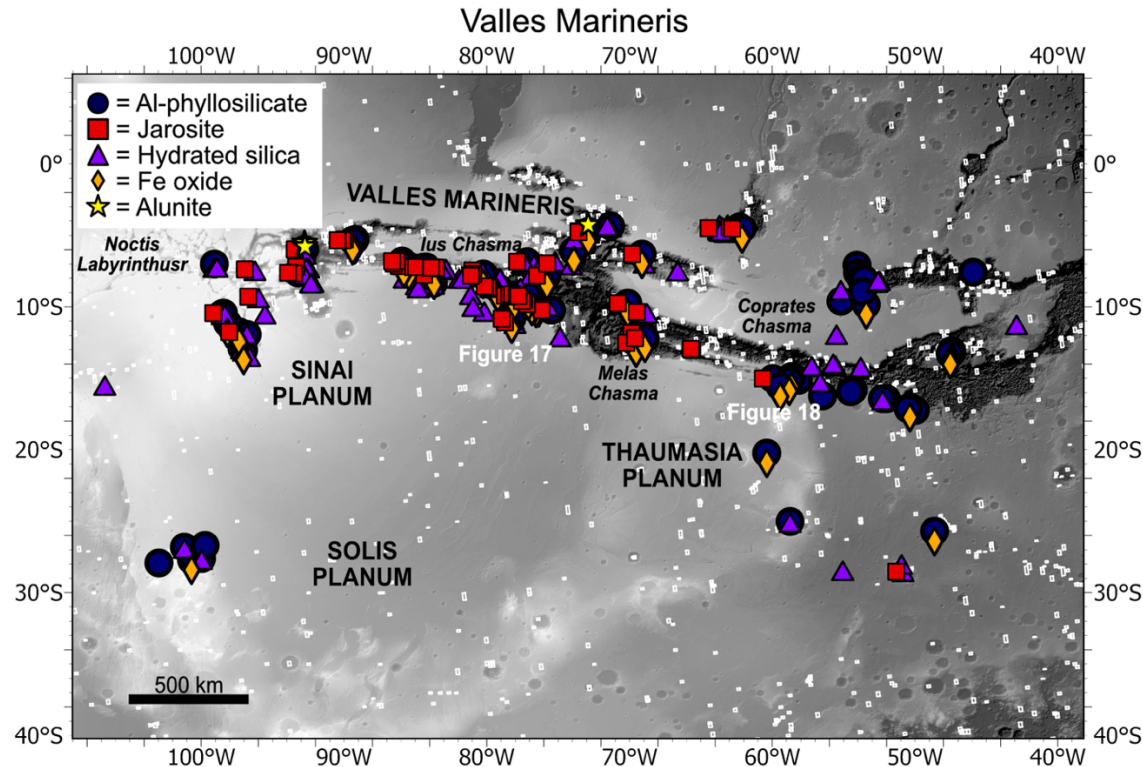


Figure 16: Distribution of detections of Al-phylllosilicate, jarosite, alunite, hydrated silica, and Fe oxide (where it is detected in Al-phylllosilicate-bearing images) in Valles Marineris within CRISM MTRDR images (footprints in white). The locations of subsequent figures 17 and 18 are labeled. The basemap is the MOLA interpolated DEM (USGS).

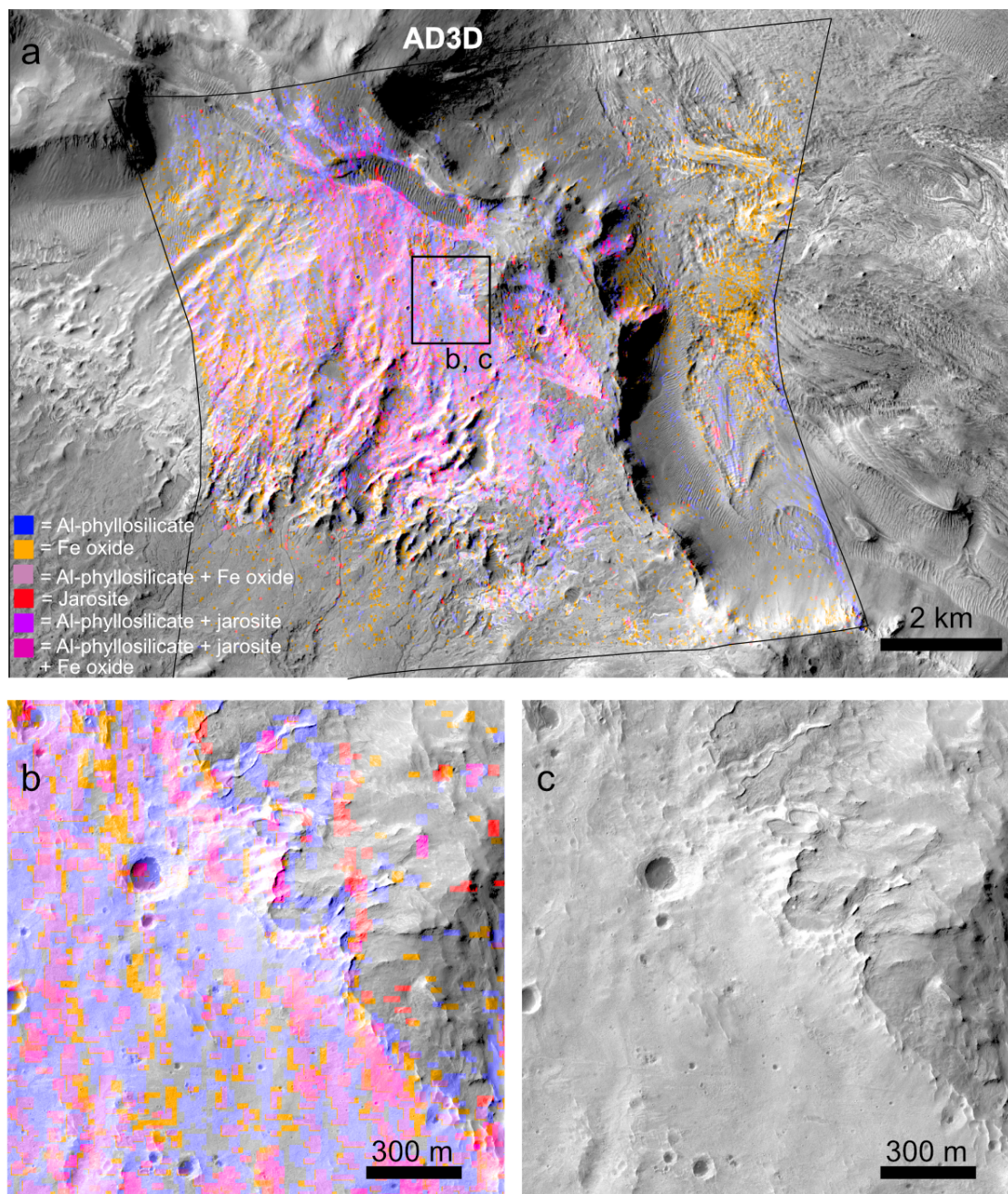


Figure 17: a) The full mineral map of the image FRT000AD3D showing Al-phyllsilicate, jarosite, and Fe oxide within Ius Chasma b, c) Al-phyllsilicate, jarosite, and Fe oxide are well-mixed in a smoother layer that apparently drapes the underlying topography, as shown by the contact between this unit and the underlying spectrally-bland material.

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

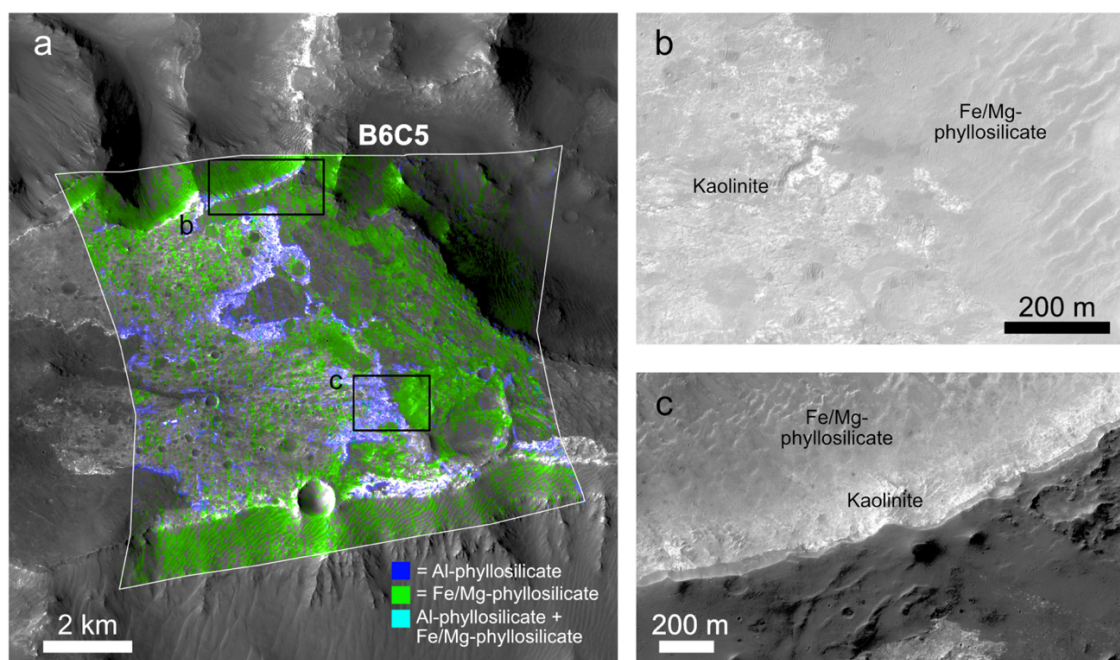


Figure 18: a) The full mineral map of the image FRT000B6C5 showing Al-phyllsilicate and Fe/Mg-phyllsilicate in a plateau and chasm walls within Coprates Chasma. b) Close-up example of the contact between Al-phyllsilicate—kaolinite in this case—and Fe/Mg-phyllsilicate. The kaolinite unit is light-toned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

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

Jarosite and Fe oxide are abundant throughout Valles Marineris. In western Valles Marineris, these minerals are frequently mixed with Al-phyllsilicate and hydrated silica in the thin layer draping underlying topography. In this region, these three alteration minerals appear intimately mixed (e.g. Figure 17). Three images were found to contain alunite: we corroborated detections of alunite in FRT0000A48D and FRT00009180

(Viviano et al., 2013) and found a new detection in FR0000A86A (Figure 16). These alunite deposits are observed mixed with Al-phyllsilicate and hydrated silica in images that also contain jarosite, and all were found within the interior of the chasms. There is an evident positive correlation between jarosite-alunite and Fe oxide occurring preferentially alongside Al-phyllsilicate deposits that are deeper in the interior of the chasms. In eastern Valles Marineris, where Al-phyllsilicate is primarily observed at higher elevations on plateaus or the plains surrounding the chasms, jarosite and Fe oxide are sparser, and the Al-phyllsilicate typically lacks these associated alteration phases (Figure 16).

4.3.2.5 Mawrth Vallis

The nature of the phyllosilicate stratigraphy in Mawrth Vallis has been much examined and much debated since hyperspectral imagery of it was first acquired. Our analysis of this region is also ambiguous, but it appears that multiple Al-phyllsilicate formation processes may have been present over its long alteration history, as we observe characteristics that appear consistent with both the Al-phyllsilicate stratigraphy we observe in Hellas Planitia/Eridania Basin and that which we observe in Nili Fossae/Libya Montes/Terra Sirenum/Valles Marineris.

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

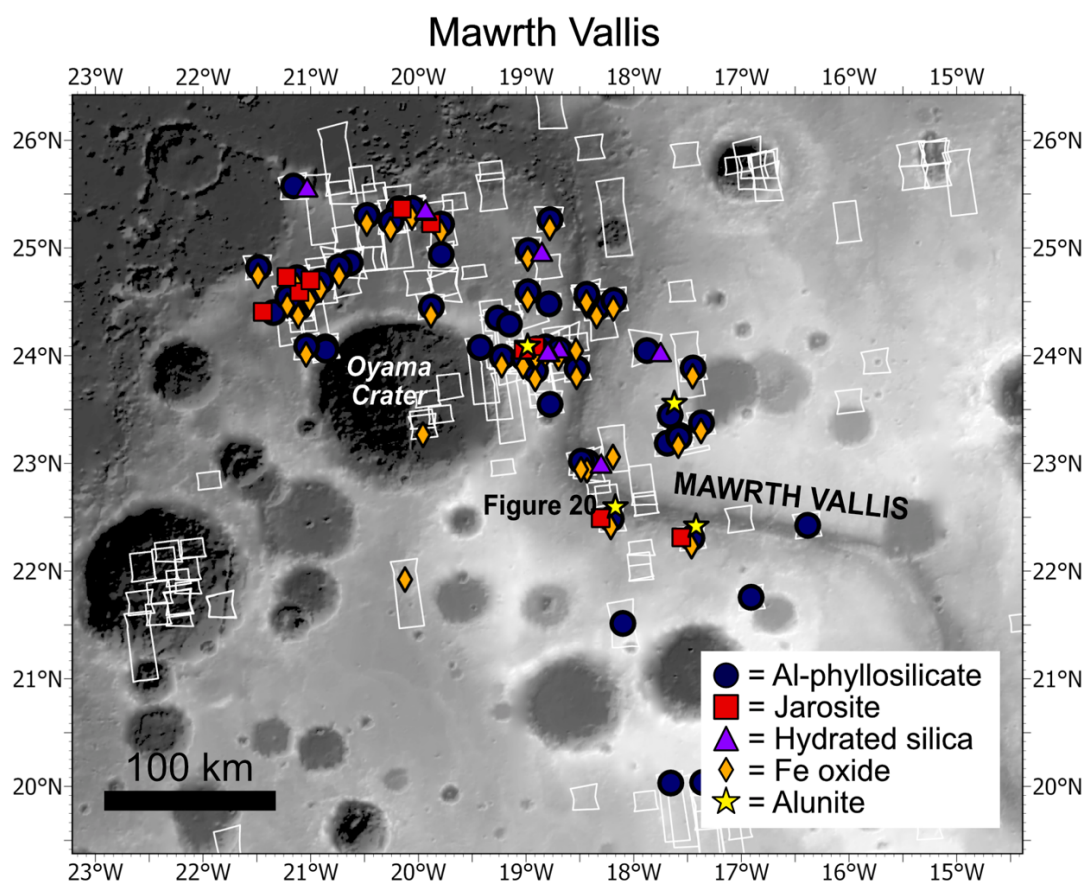


Figure 19: Distribution of detections of Al-phyllsilicate, jarosite, hydrated silica, and Fe oxide (where it is detected in Al-phyllsilicate-bearing images) in Mawrth Vallis within CRISM MTRDR images (footprints in white). The location of subsequent figure 20 is labeled. The basemap is the MOLA interpolated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

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

phyllosilicate where it contacts spectrally bland material. This bland material may indicate sand accumulation in local topographic lows, which jarosite exposed on the edges of these lows (Figure 20b). The contact between the Al-phyllosilicate and Fe/Mg-phyllosilicate is sharp along parts of the contact, with a clear color difference between the minerals. The Al-phyllosilicate has m-scale polygonal fractures, and the texture of the Fe/Mg-phyllosilicate varies from smooth to a similar polygonally fractured texture. Along portions of the contact, the transition from one phyllosilicate to the other appears more gradational, though a clear color difference between them remains (Figure 20c).

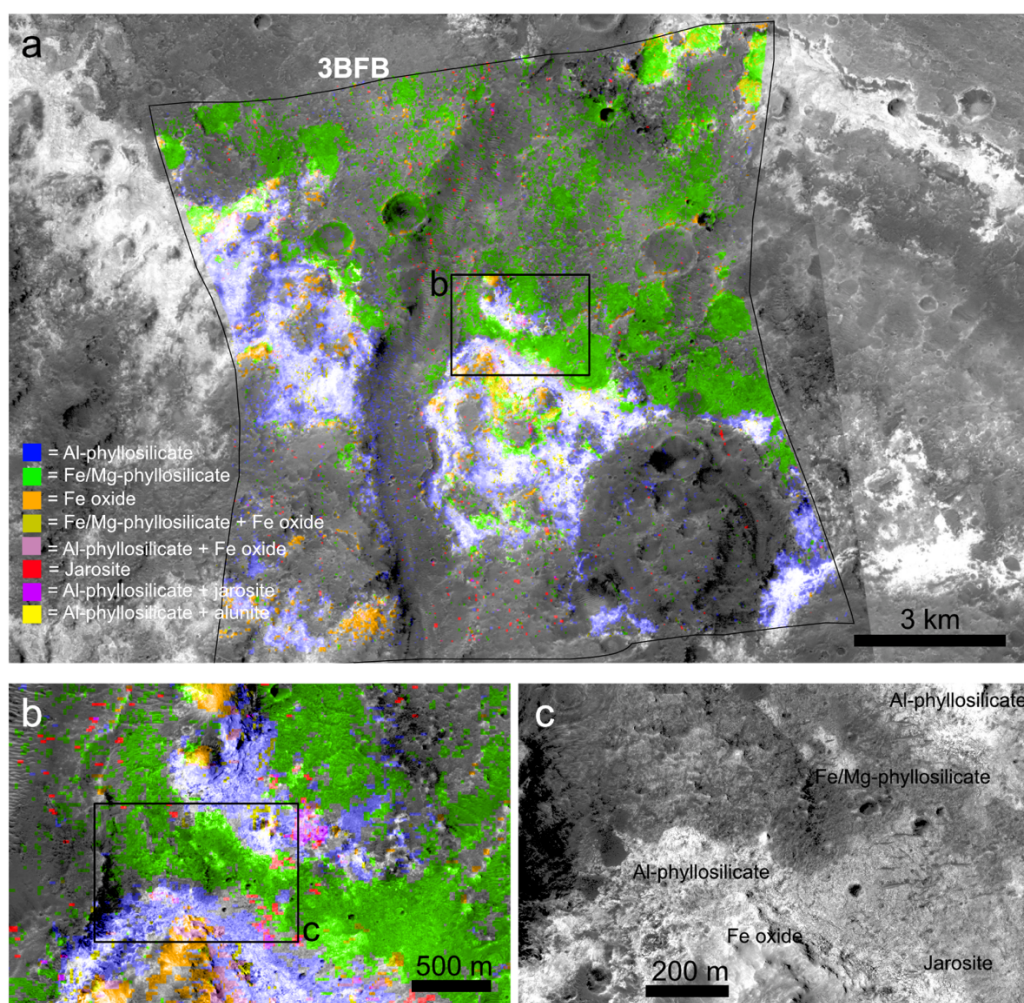


Figure 20: a) The full mineral map of image FRT0003BFB showing Al-phyllosilicate, Fe/Mg-phyllosilicate, jarosite, alunite, and Fe oxide on a slope adjacent to Mawrth Vallis. b) Close-up of the distribution of these alteration minerals. Al-phyllosilicate overlies Fe/Mg-phyllosilicate. Fe oxide overlies Al-phyllosilicate and mixes with it at the contact.

Jarosite is mixed with Al-phyllsilicate largely near the contact with Fe/Mg-phyllsilicate. c) Close-up demonstrating the textures and contacts of these minerals. The Al-phyllsilicate unit is light toned with m-scale polygonal fractures, and the Fe/Mg-phyllsilicate is darker toned but with a similar texture.

5 Discussion

5.1 Formation of Al-phyllsilicate and associated minerals

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

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

Of the six regions we examined, Al phyllsilicate formation by basalt weathering is the most consistent process for our observations of the Al-phyllsilicate stratigraphy at Hellas Planitia and Eridania Basin in western Terra Sirenum. In Hellas Planitia, Al-phyllsilicate and Fe/Mg-phyllsilicate are frequently mixed at the CRISM resolution of 18 m/pixel. Where these minerals occur in the same image, the two phyllsilicates

typically have similar textures (Figure 6, 7) and lack sharp contacts. This textural similarity and spectral mixing indicate that they formed from the same protolith, consistent with the conclusions of Carter et al. (2015).

As expected for leaching of basalt under oxidizing conditions (Nesbitt and Young, 1989; Gaudin et al., 2005; Greenberger et al., 2012; Blesa and Maroto, 1986), Fe oxide is found alongside much of the Al- and Fe/Mg-phylllosilicate in Hellas Planitia and Eridania Basin. In Hellas Planitia, we observe Fe oxide apparently intimately mixed throughout the Al-phylllosilicate to Fe/Mg-phylllosilicate weathering sequence exposed in 13D3A, as well as elsewhere in the image where it occurs on its own not mixed with any other detectable phases (Figure 6). We do not detect any jarosite or alunite in this region, which suggests that the alteration occurred under more neutral pH conditions. In Eridania Basin, we detect sparse alunite alongside Al-phylllosilicate and jarosite alongside both Al-phylllosilicate and Fe/Mg-phylllosilicate. This indicates a period of acidic alteration, either the original alteration of basalt to form these phylllosilicates or a later period of acidic fluid interaction.

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

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

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

In the other regions of Mars that we examined here, the Al-phylllosilicate does not appear to be consistent with formation from a basaltic protolith as part of a leaching sequence. In Nili Fossae, Libya Montes, eastern Terra Sirenum, and Valles Marineris, the

Al-phyllsilicate is better explained by formation from alteration of a volcanoclastic material like an ash.

In these regions, where Al-phyllsilicate and Fe/Mg-phyllsilicate occur adjacent to each other, they correspond coherently to units with distinct textures. In Nili Fossae, Libya Montes, and Terra Sirenum, Al-phyllsilicate is often layered or exposed in sedimentary plateaus that are consistent with formation from a transported sedimentary material (Figure 11, 12, 14, 15). In contrast, the Fe/Mg-phyllsilicate in these regions is unlayered. In Valles Marineris, much of the Al-phyllsilicate occurs in a unit that appears to be draped over the underlying topography and lacks exposed associated Fe/Mg-phyllsilicate (Figure 17). Where the contact between these minerals is exposed, there is no mixing, and it appears unconformable. This is consistent with formation of the Al- and Fe/Mg-phyllsilicates from two distinct protoliths.

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

We find a diversity of Al-phyllsilicate compositions within and between regions examined here (Figure 1, 2). While most regions contain both kaolinite and montmorillonite as well as other aluminosilicate compositions, we find that for these

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

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

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

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

The conditions necessary to form jarosite are: sufficient Fe and S, pH of 1.5–4.5 (Symonds et al., 1994; Poulet et al., 2009; Ehlmann et al., 2016), and oxidizing conditions. To form alunite, low pH is required alongside sufficient Al^{3+} (Symonds et al.,

1994). Therefore, if there was widespread regional circulation of acidic fluids, we would expect this acidic alteration to form jarosite in association with Fe-phyllsilicates (supplying the requisite Fe), while alunite would form in association with Al-phyllsilicates (supplying the requisite Al). It is therefore surprising that in these regions, jarosite is almost always associated with Al-phyllsilicate and never with Fe/Mg-phyllsilicate. This suggests that the conditions necessary to form jarosite are met in conjunction with the Al-phyllsilicate in these regions but not with the Fe/Mg-phyllsilicate. We argue that if the Al-phyllsilicate protolith, which is distinct from the Fe/Mg-phyllsilicate protolith in these regions, was S-bearing, the observed jarosite could be produced through interaction of this protolith with Fe-bearing water. A geochemically distinct, S-bearing, aluminous sedimentary Al-phyllsilicate protolith is most consistent with a volcanic ash. Because Fe is required to form jarosite and the Al-phyllsilicate units in these regions largely lack other Fe-bearing minerals, we propose that Fe-enriched fluid could be produced by leaching Fe out of the Fe/Mg-phyllsilicate that underlies the Al-phyllsilicate in these regions. When this Fe-bearing water interacts with the S-bearing Al-phyllsilicate protolith, jarosite can precipitate. Alunite may have formed where the water interacting with the volcanic ash was less Fe-enriched, and the local Al combined with local S to produce alunite.

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

formed during the final stages of significant water interaction. Where there is substantial Fe oxide alongside jarosite, there was likely continued aqueous alteration after the formation of jarosite.

5.1.3 Mawrth Vallis, a special multi-process case?

Unlike the other regions examined here, the mineralogy and stratigraphy observed in Mawrth Vallis does not appear to be consistent with either Al-phylllosilicate formation solely through pedogenic leaching of basalt or solely through alteration of an aluminous volcanic ash, but rather has elements consistent with both. As expected with formation as a pedogenic leaching sequence under oxidizing conditions, we find that much of the Al-phylllosilicate in Mawrth Vallis is mixed with Fe oxide (Figure 19). Additionally, in some locations, the texture of Al-phylllosilicate is similar to that of the underlying Fe/Mg-phylllosilicate, and the contacts between them appear possibly gradational. However, in other locations, there do appear to be sharper contacts between the Al- and Fe/Mg-phylllosilicates, more consistent with formation from two distinct protoliths (Figure 20c).

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

Because we observe elements consistent with both formation theories, we propose that both could have influenced the formation of Al-phylllosilicate in Mawrth Vallis. Bishop et al. (2008) find that the Al-phylllosilicate in this region is composed of two distinct units, a kaolinite unit overlying a montmorillonite unit. This compositional diversity may be consistent with our proposed formational diversity, as we find a possible association of montmorillonite predominance with regions of basaltic leaching and kaolinite predominance with volcanic ash alteration. Klidas et al. (2025) find that the true thicknesses of the Al-phylllosilicate units in Mawrth Vallis are consistent with

draping over the landscape, either from top-down pedogenic leaching or an airfall deposit. Both could have produced the observed geometry.

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

If many of the Al-phyllsilicate-bearing regions formed from a volcanic ash as we propose, some of the possible volcanic sources are clear while others are ambiguous. There is no clear evidence for volcanoes in Nili Fossae or Libya Montes, but ash could have been sourced from the large adjacent Syrtis Major volcano (Kerber et al., 2013; Fawdon et al., 2015; Robbins et al., 2011). Additionally, fissure volcanism can lack an easily detectable geomorphic signature at the surface but could be the source of these pyroclastics. Ash deposits are expected to be thicker at closer distances to their source volcanoes. In Nili Fossae, few Al-phyllsilicate deposits could be measured, but there is no clear directional pattern in the measured apparent thicknesses that indicates the volcanic source (Baker and Ehlmann, in review). This may indicate the effects of post-depositional reworking of the ash to accumulate in topographic lows. In Terra Sirenum, the apparent thicknesses of the Al-phyllsilicate thin with increasing distance from the volcano Arsia Mons, which suggest that that volcano is its volcanic source (Leask et al., 2024). In Mawrth Vallis, the thickness of the Al-phyllsilicate does not increase monotonically in a direction that points to its source, but the measured thicknesses do indicate that it is in a unit that is draped across the underlying topography in the region, consistent with an airfall deposit (Klidaras et al., 2025).

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

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

Our analysis of Al-phyllsilicate formation also suggests that these ash deposits are more evolved than basaltic or otherwise mafic compositions. Mars is dominantly mafic in composition (e.g. Christensen et al., 2000; McSween, 2009), though a growing body of research suggests the presence of localized evolved (i.e., more felsic) compositions (e.g., Christensen et al., 2005; Wray et al., 2013; Rogers and Farrand, 2022; Phillips et al., 2022). These evolved rocks, which are widespread on Earth, form through either subduction zone dynamics or fractional crystallization in a magma chamber. While Mars was not thought to have plate tectonics, fractional crystallization appears to be a distinct possibility to produce evolved lavas (Udry et al., 2018; Pieterek et al., 2026). Periods of silicic lava production would be expected to produce more explosive eruptions (Fink and Manley; 1989; Castro et al., 2014) which could have delivered the Al/Si-rich volcanoclastic Al-phyllsilicate protolith across Mars.

6 Conclusions

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

We conclude that our observations are most consistent with Al-phyllsilicate formation from two distinct processes across Mars. In northern Hellas Planitia and the Eridania Basin region of Terra Sirenum, we find that Al-phyllsilicate and the underlying Fe/Mg-phyllsilicate have similar textures. These textures vary with location from m-scale polygonal fractures to layers to smoother units, but the phyllsilicates are texturally

similar to each other wherever they occur in these regions. Fe oxide is frequently mixed with both Al- and Fe/Mg-phylllosilicate, and jarosite and/or alunite is detected alongside both phylllosilicates in Eridania, though these sulfates are absent from Hellas Planitia. We conclude that these results are most consistent with the formation of Al-phylllosilicate from a pedogenic leaching sequence from a single basaltic protolith under oxidizing conditions.

In contrast, our observations of Al-phylllosilicate elsewhere on Mars do not appear to be consistent with formation from pedogenic leaching of basalt. In Nili Fossae, Libya Montes, eastern Terra Sirenum, and Valles Marineris, Al-phylllosilicate appears to be distinct from Fe/Mg-phylllosilicate. These units differ in texture, and where their contact is exposed, it tends to be sharp and unconformable. Where jarosite and alunite occur in these regions, they are strongly spatially associated with Al-phylllosilicate and never associated with Fe/Mg-phylllosilicate. Most Al-phylllosilicate in these regions lacks associated Fe oxide with the exception of Valles Marineris, where continued alteration may have caused reprecipitation of jarosite as Fe oxide. The Al-phylllosilicate stratigraphy in Mawrth Vallis has elements consistent with both proposed formation processes, and we conclude that it most likely represents the combined effects of both processes operating in the region at different times.

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

These results suggest that the extensive aqueous alteration required to produce Al-phylllosilicate from a basaltic protolith likely was not widespread across Mars. Instead, it was concentrated in only a small number of locations. Elsewhere, Al-phylllosilicate could have formed with an order of magnitude less cumulative contact with water. The Al-

phyllosilicate units we interpret to have formed from aluminous ash also suggest more widespread explosive and evolved volcanism than previously thought.

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Open Research

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

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*Chapter 4*REMOTE SENSING WATER TEMPERATURE IN PERMAFROST
RIVERINE CORRIDORS**Samantha R. Baker¹ and Michael P. Lamb¹**

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Abstract

Water temperature in rivers and floodplains impacts numerous processes including fisheries, ecosystem health, and geochemical cycling and is of particular concern in Arctic environments with rapidly changing temperatures and thawing permafrost. Remote sensing provides contiguous spatial coverage globally but is an underutilized resource for Arctic rivers and wetlands, which often lack in situ data like temperature gauges. We used the remotely sensed 100 m/pixel Land Surface Temperature dataset from Landsat to investigate water temperature maps of riverine corridors in Alaska. We examined three diverse locations in the Yukon River watershed: a typical anastomosing stretch of the Yukon River, the confluence of the Yukon and Tanana rivers, and the meandering Koyukuk River. We created spatially contiguous, accurate (median error of 0.46°C) water temperature maps for these bodies of water > 210 m in width. We demonstrated how water temperature acts as an indicator for floodplain hydrodynamics. We find that, due to turbulent mixing, river temperature from space accurately captures values at depth. River water temperature can trace the mixing of tributaries tens of km from the confluence and shows connectivity, mixing, and stratification of oxbow lakes. Additionally, the surface temperatures of adjacent thermokarst lakes can differ from each other by 5°C likely indicating disruption from lake thermal stratification by intermittent mixing events. We discuss future applications of remote sensed river water temperature for understanding thermal refuges and stresses on salmon populations, predicting thaw-limited river erosion rates, and guiding in situ sensor placement for hydrologic and geochemical studies of changing permafrost environments.

Plain Language Summary

Water temperature plays a critical role in riverine wetlands environments, particularly in the Arctic, where permafrost thaw, chemical cycling, and fishery populations are of concern. River water temperature is typically measured by gauges placed in the water at key locations, but gauges are scarce in the remote Arctic and do not fully capture the

complex distribution of temperature in wetlands environments. We therefore explore using remotely sensed temperature data measured by the Landsat satellites, for which there is complete global coverage, to create surface water temperature maps for three locations in the Yukon River watershed, the largest river in Alaska. Examining their temperatures in late May just after the ice melts, in August, and in October before the ice freezes, we found that for water bodies with widths >210 m, the Landsat data is typically accurate to $<1^{\circ}\text{C}$. We highlight several capabilities of these maps, including illustrating wetland hydrodynamic processes and varying controls on river temperature across seasons. We demonstrate that these remotely sensed data can be utilized to fill a critical gap in our study of Arctic riverine environments and are integral to understanding important processes in the Arctic, including ecosystem health, greenhouse gas emission, and river erosion.

1 Introduction

The Arctic and subarctic regions are at the forefront of the Earth's changing climate, with rapid changes happening in river corridors. Arctic amplification is causing this region to experience the highest levels of air temperature warming in the world from anthropogenic effects, up to 4 times that of mean global trends (Burn and Kokelj, 2009; Romanovsky et al., 2010; Post et al., 2019). These changes in air temperatures result in warming inland waters with direct impact on hydrologically interconnected river–wetland systems that include abundant tie channels, sloughs, thermokarst lakes and oxbow lakes with highly variable river connectivity (Smith et al., 2005; Grosse et al., 2013). Numerous small lakes, many adjacent to rivers and in the path of their erosion, create a wetland environment that is rapidly changing, highly water temperature-sensitive, and challenging to monitor. Basic questions are difficult to answer: for example, are there significant variations in water temperature between large river channels and their neighboring sloughs, thermokarst lakes and oxbow lakes?

Warming river floodplain systems influences many processes on the frontlines of Arctic change such as permafrost thaw, river erosion, fisheries, and biogeochemical fluxes. For example, river erosion for some permafrost-bearing banks is accelerating (Geyman et

al., 2024), endangering infrastructure and nearby communities, and is controlled primarily by increasing river water temperature (Costard et al., 2003; Douglas et al., 2023). These increased bank erosion rates have a cascading effect on the environment by releasing long-frozen bank material that can contain carbon (Douglas et al., 2022; Lininger and Wohl, 2019) and toxic heavy metals (Miner et al., 2021; Smith et al., 2024).

In addition, river temperature has a major impact on fish. In Alaska, salmon migrate annually from the Pacific Ocean up rivers in the Arctic and subarctic to their breeding grounds, and they are exceptionally temperature sensitive. Salmon have been found to have a preferred water temperature of around 15°C (Eliason et al., 2011). At temperatures above 20–28°C, they do not have enough energy to continue swimming and do not survive the migration (Frechette et al., 2018). Salmon that are under thermal stress may be able to survive by visiting thermal refuges, local regions of anomalously lower water temperature. These thermal refuges include intersections with colder tributaries and confluence plumes, groundwater seeps, pools that are sufficiently stagnant to achieve some thermal stratification, and hyporheic exchange (Bilby, 1984; Ebersole et al., 2003; Torgersen et al., 2012). Despite this, some salmon populations have declined dramatically over the past several decades, causing economic hardships for both the commercial industry and Indigenous subsistence fishers (e.g. Biela et al., 2022).

Water temperature in the Arctic is also a critical component of concerns about geochemical fluxes such as feedback loops with greenhouse gas release from rivers and lakes. Inland waters are significant net sources of CO₂ to the atmosphere from biotic respiration and photosynthesis (Cole et al., 1994; Sobek et al., 2005; Kosten et al., 2010), and Arctic lakes are particularly high emitters of CO₂ and CH₄ due to permafrost thaw (Serikova et al., 2019; Zandt et al., 2020; Zabelina et al., 2021). The controls on the quantity of CO₂ from rivers and lakes are not fully understood, but temperature plays a significant modulating role with higher temperatures leading to greater CO₂ release (Åberg et al., 2007; Kosten et al., 2010; Striegl et al., 2012; Ford et al., 2024). It is therefore necessary to understand the water temperature across Arctic landscapes to better model and predict the release of further greenhouse gases from this environment.

Monitoring water temperature changes in permafrost rivers and their surrounding wetlands has been challenging owing to the immense size and remoteness of the Arctic and subarctic. The primary method of measuring river temperature is with in situ temperature probes placed at river monitoring stations (e.g. Kaushal et al., 2010; Isaak et al., 2012; Wrzesiński and Graf, 2022). While these gauges have been an essential tool in tracking river temperature, they are limited in coverage, as they only measure local water temperature and are typically sparsely placed. Moreover, these gauges tend to be placed along large primary channels and do not capture the diverse web of riverine wetland environments (Krabbenhof et al., 2022). There are major efforts underway to fill this data gap, including the University of Alaska AKTEMP Water Temperature Database – a database of river temperature records from short-term in situ gauges from across the state. While this dataset expands the quantity and hydrologic diversity of in situ gauges, it is still limited in its coverage.

Thermal remote sensing offers a means to partially fill this data gap. While airborne and drone-based studies can provide high spatial resolution (e.g., <15 cm/pixel), such studies are necessarily limited to small study areas and are difficult to implement in remote areas of the Arctic (e.g., Wawrzyniak et al., 2013; Frechette et al., 2018). In contrast, for the past 40 years, satellites have been providing contiguous spatial coverage of global surface thermal emission, which can be converted to surface water temperature in the Arctic and subarctic. In particular, the Land Surface Temperature (LST) dataset is produced from Landsat 4–9 thermal emission data ranging from 120–60 m/pixel in resolution and dating back to 1982 (Cook et al., 2014; EROS, 2020). While satellite-based remote sensing has commonly been used to measure sea surface temperature (e.g. Prabhakara et al., 1974; Minnett et al., 2019) and large lakes (e.g. Layden et al. 2015; Piccolroaz et al., 2024), it has been used less for rivers.

Important previous work has focused on tropical and temperate settings including using LST or bespoke Landsat-derived surface temperatures to quantify the effects of tributaries on water temperature of the Rhône River (Wawrzyniak et al., 2012) and a stretch of the Ganges River (Das et al., 2022). Additionally, Wang et al. (2025) use the Landsat-derived surface temperature to examine the spatial and temporal variation of water

temperature on the Yarlung Tsangpo River. LST also has been used to quantify local anthropogenic effects on river temperature including from the dams on the Yangtze River (Ling et al. 2017; Shi et al., 2021) and thermal pollution from hydroelectric plants in Brazil (Alcântara et al., 2010) and France (Wawrzyniak et al., 2012). LST has recently been applied to quantify the decadal-scale warming trends in stretches of the Ganges (Kachari et al., 2024) and Amazon (Santos Fleischmann et al., 2025) rivers. One of the few studies in permafrost terrains to use LST was a validation of the method against an in situ USGS gauge at Pilot Station by Baughman and Conaway (2021), who found mean error of 0.47°C, demonstrating that seasonal trends should be readily measurable.

Here we present an exploratory study to use the LST data to examine spatial and temporal patterns of river and wetland surface water temperature and connectivity at three example study sites along the Yukon River in Alaska. Taking this approach to the Arctic and subarctic poses additional considerations due to extreme seasonality, the complexity of river-wetland systems, and their hydrological connectivity (e.g., Farquharson et al., 2016). Previous studies of remote sensing water temperature have not examined the relationship between river temperature and that of floodplain wetlands, but this holistic view is important in a thermokarst landscape. We have some, but limited, in situ data at these study locations. Here, we do not provide a complete hydrological study of rivers and wetlands, nor do we attempt to test hydrological or thermal models. Instead, as one of the first applications of LST to permafrost river corridors, we demonstrate how remote sensing can be used to generate accurate and spatially continuous seasonal water temperature maps for Arctic wetlands environments, revealing a rich pattern of hydrological connectivity across these dynamic environments.

2 Study Location and Methods

2.1 Study locations

We use the LST dataset to examine how water temperature varies spatially and seasonally in permafrost river corridors. We selected three example locations to span

diverse hydrologic contexts along the Yukon River watershed in discontinuous permafrost where change is currently rapid. We examined the meandering Koyukuk River, a major tributary of the Yukon River, near the village of Huslia; the confluence of the Yukon River and the Tanana River near Tanana town; and the anastomosing Yukon River near Beaver, AK (Table 1; Figure 1).

Name	Center coordinates	Description
Huslia	65.76°N, -156.36°E	Single-threaded meandering stretch of the Koyukuk River, a major tributary of the Yukon River
Tanana town	65.18°N, -152.63°E	Intersection of the multi-threaded Yukon River and the Tanana River
Beaver	66.345°N, -147.40°E	Multi-threaded anastomosing stretch of the Yukon River midway along its length, representative of much of the river

Table 1: Descriptions of study locations.

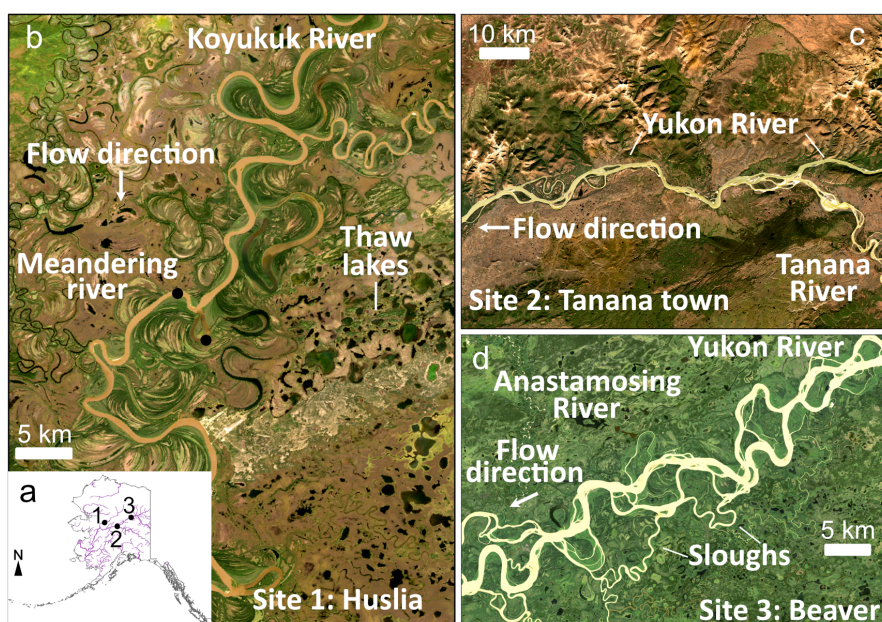


Figure 1: a) Study locations in the Yukon River watershed shown on an outline of the state of Alaska. b–d) Landsat enhanced color visible RGB images of each study location. For each site, some types of fluvial geometry are listed (e.g., meandering, anastomosing), key hydrologic features are identified, and the flow direction of the river is indicated. North is up for all panels. The two black dots indicate the locations of in situ water temperature loggers.

2.2 Landsat derived temperature data

The remote sensing data in this project comes from Landsat 8 Operational Land Imager (OLI) level 2 data products. We used visible–near-infrared (VNIR) reflectance products that were generated with the Land Surface Reflectance Code (LaSRC) algorithm (Vermote et al., 2018) and the Land Surface Temperature data products generated from infrared thermal emission measurements (Cook et al., 2014). Surface temperature data were derived from the thermal emission band. For Landsat 4, 5, and 7, this is one band from 10.40 - 12.50 μm . For Landsat 8 and 9, there are two thermal emission bands at 10.60 - 11.19 μm and 11.50 - 12.51 μm . The amount of energy emitted from a surface at a given wavelength is dependent on its temperature and its emissivity, which is the ratio of energy that is absorbed and re-emitted to the energy that is instead reflected at that wavelength. The emissivity therefore describes the deviation of the material from a perfect blackbody, where all light is emitted, and so the emissivity is equal to 1. This relationship is described by the Stefan-Boltzmann equation:

$$T = \frac{hc}{\lambda k_B \ln \left(\frac{2hc^2}{B\lambda^5} + 1 \right) \epsilon} \quad (1)$$

where h is Planck's constant, c is the speed of light, λ is the wavelength considered, k_B is the Boltzmann constant, B is the radiance at the given wavelength (this is the thermal emission measured by Landsat), and ϵ is the emissivity.

The derivation of temperature from radiance to create the LST dataset is based on this physics with further correction and processing. The effects of atmospheric radiance and scattering are removed as described by Barsi et al. (2014) and Cook et al. (2014). Because Landsat measures only the thermal emission, the surface emissivity must also be known for temperature to be derived (equation 1). Mean monthly emissivity for each pixel was calculated from the Advanced Spaceborne Thermal Emission and Reflectance radiometer (ASTER) multi-band thermal emission data combined with normalized

difference vegetation index (NDVI) measurements from the contemporaneous visible–near-infrared Landsat spectral bands as described by Hulley et al. (2012). We find that water is consistently assigned an emissivity of 0.9904. This method of temperature retrieval measures the temperature of approximately the top 10 cm of the water (Handcock et al., 2012).

2.3 Creation of water-only masks for temperature-mapping

For each location of interest, we identified several cloud-free scenes from Landsat 8 across the unfrozen season. We chose an image in May soon after ice breakup, one in August, and one in October before river freezing. We selected only Landsat 8 images to remove any complications that could be introduced by comparing data across Landsat instruments that vary in resolution. The thermal data used for the location of interest maps have a resolution of 100 m/pixel. Landsat 8 began data collection in 2013, and it has an imaging repeat rate of around 2 weeks. This means that any given location has been imaged approximately 350 times by this instrument. To compare images equally and remove the possibility of clouds and cloud shadow affecting or obscuring temperature patterns, we hand-selected only images that completely lacked cloud cover in the area of interest. Because Alaska is a cloudy region, this reduced the number of usable images available for a given season in each location to typically <5 . We therefore were limited in clean data availability and so selected a single image for each season that demonstrates the pattern of water temperature across the environment at that time.

For each image, we created a water mask using the method described by Zou et al. (2018) using OLI’s visible–near-infrared reflectance bands and the quality assessment band. To be considered water, a pixel must meet the following criteria:

1. Free of cloud cover as defined by Landsat’s quality assessment
2. Modified Normalized Difference Water Index (mNDWI) $>$ Enhanced Vegetation Index (EVI) or Normalized Difference Vegetation Index (NDVI)
3. $EVI < 0.1$

The definitions of NDVI, mNDWI and EVI are:

$$\text{NDVI} = \frac{R_{\text{near-infrared}} - R_{\text{red}}}{R_{\text{near-infrared}} + R_{\text{red}}} \quad (2a)$$

$$\text{mNDWI} = \frac{R_{\text{green}} - R_{\text{shortwave infrared}}}{R_{\text{green}} + R_{\text{shortwave infrared}}} \quad (2b)$$

$$\text{EVI (for Landsat 8)} = \frac{2.5(R_{\text{near-infrared}} - R_{\text{red}})}{R_{\text{near-infrared}} + 6(R_{\text{shortwave infrared}}) - 7.5(R_{\text{blue}}) + 1} \quad (2c)$$

where R_x is the reflectance in the x band (e.g., R_{green} is the reflectance in the green band). We also masked out some remaining snow by hand.

We use this water mask to isolate the temperature data to only the water temperature in the scene. We examined each generated temperature map to exclude those with obvious artifacts such as stripes across the image. Once we identified artifact-free images for each site of interest, we examined these maps by hand to identify qualitative patterns in water temperature across these diverse riverine environments.

An important limitation on the utility of this dataset for generating spatially resolved temperature maps is the disparity between the available resolution of the LST images and the inherent resolution of the Landsat thermal bands. While Landsat 8 thermal band has a resolution of 100 m, all processed LST data has been resampled to 30 m/pixel using a nearest-neighbor interpolation to match the resolution of the Landsat VNIR bands (USGS, 2025). Therefore, while the water masking is accurate to 30 m/pixel, the temperature values that match each masked water pixel do not necessarily correspond to entirely water because the calculation of its temperature value could have included interpolation from surrounding land temperature.

This trend is evident from the raw masked temperature images where there appears to be a clear cross-sectional variation in river temperature (Figure 2). This is not reflective of the reality of the water temperature, as these rivers are fully turbulent, and

therefore temperature is well-mixed across their profile (e.g. Villamizar et al., 2014).

Land and water temperatures can vary substantially due to thermal stratification of the water, how water is sourced from far-reaching environments, and their differing material properties such as specific heat. Because water has a higher thermal inertia than land (i.e., vegetation, rock, and soil), the water in Alaska is colder than the surrounding land in the spring. In the fall, this trend reverses, as water cools more slowly and therefore remains warmer than the land.

To correct for this, we processed the masked LST images to remove 3 pixels from all water edges, as these pixels could have substantial mixing with the land temperature signal. These processed images do not demonstrate this same cross-sectional trend (Figure 2). The necessity for this step limits the size of water features that can be examined with this method. These results suggest that water features must be at least 7 Landsat VNIR pixels (that is, 210 m) across to achieve an accurate temperature signal. Therefore, the method described here of generating spatially resolved water temperature maps can only be applied to especially wide rivers as well as larger ponds.

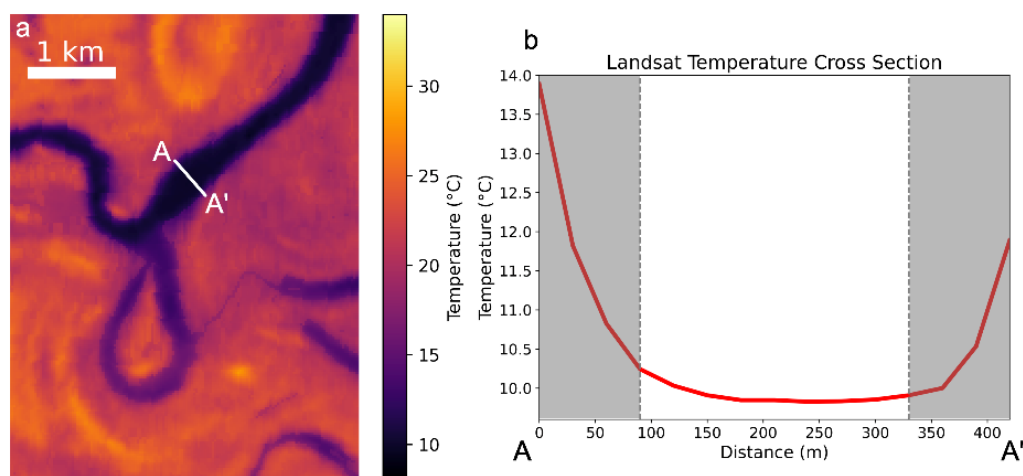


Figure 2: a) Temperature map of a short stretch of the Koyukuk River showing both the ground and water temperature. b) The temperature profile of the segment identified as water in the cross-section. The gray shaded regions indicate the temperature values of the pixels removed from the water temperature maps due to mixing with the land temperature signal.

For all following temperature maps, we show both the masked water temperature and the full water extent. The pixels within the filtered water mask, those for which we are confident the LST dataset is providing the temperature of water with no land signal, are assigned a temperature value and a color based on that map's color scale. These data are plotted on top of a binary map of our full 30 m/pixel water mask generated from Landsat TM bands as described above. This binary map is plotted in black and white, and it demonstrates the full extent of the water in the image detectable by Landsat to provide context to the distribution of water in the scene.

Additionally, the temperatures maps for each region are plotted with two colorbars. For the first, all images are plotted with the colorbar scaled to 0–17°C. This demonstrates at a glance the absolute change in temperature of a location across seasons. For the second, each temperature map is plotted with a divergent colorbar where the middle (white) is centered on the mean water temperature in the visible extent, and the scale limits are $\pm 5^\circ\text{C}$ from that mean. The values plotted in both versions of each map are temperature, but the divergent scale better illustrates the relative temperature variation within a scene.

2.4 Comparison to other data

To ground truth the data, Baughman and Conaway (2021) performed a comparison between the LST temperature and in situ temperature measured at the USGS Pilot Station monitoring station on the Yukon River, and they found that the LST dataset is accurate with a mean difference of -0.47°C (LST temperature – in situ temperature). We corroborated these measurements by comparing the LST temperature values to water temperature measured in situ by the USGS Pilot Station gauge on the Yukon River. We defined a region of interest of approximately 3 km² of the Yukon River (Figure 3a) around the location of the gauge and calculated the mean surface water temperature for all available cloud-free Landsat 7, 8, and 9 images (though we only use Landsat 8 for our analysis, we use all available Landsat images for the validation). Landsat 7 launched in

1999, followed by Landsat 8 in 2013 and Landsat 9 in 2021. The thermal infrared bands have spatial resolutions of 60 m for Landsat 7 and 100 m for Landsat 8 and 9.

These images were all taken at around 2 PM local time, so we compared these remotely sensed temperature values to the contemporaneous 2 PM Pilot Station measurements (Figure 3b). We extracted all images of this region of interest with cloud cover <50% across the whole image as measured by the Landsat quality assurance parameter. This resulted in a dataset of 241 images. Many of these images still had cloud cover across the location of Pilot Station, and we removed all these images from the ground truth comparison. This created a cloud-free dataset of 57 images.

To better understand the vertical temperature structure of rivers and oxbow lakes, we also compared the surface water temperature measured by LST to in situ temperature measurements taken at several representative locations. We installed HOBO water level U20L-02 loggers at depth in the main channel of the Koyukuk River and in an oxbow lake near Huslia. These locations are shown in Figure 1. The reported temperature uncertainty for these loggers is $\pm 0.44^{\circ}\text{C}$, and they recorded water temperature every 15 minutes throughout the 2023 unfrozen season from May 23 to October 4. We compared the remotely sensed surface temperature to the temperature at depth in the river channel and oxbow lake.

To inform our interpretations of the controls of river temperature in these environments, we also compared the remotely sensed water temperature to local air temperature measurements and the available river discharge measurements. Near surface air temperature was extracted from thermometers located at airports adjacent to each study location. For Huslia, data were taken from Huslia Airport (station 70365526552), for Beaver, Fort Yukon Airport (station 70194026413), and for the confluence, Ralph M Calhoun Memorial Airport (station 70178026529). River discharge measurements are confined to only a few locations where there are in situ discharge gauges, so we used data from the USGS Pilot Station on the Yukon River (Gauge #15565447) as a reference value. Because of the distance between Pilot Station and the study locations, these data

do not reflect the absolute discharge at the locations of interest but are instead representative of the relative changes in discharge over the course of the season.

3 Results

3.1 Ground truthing and error assessment

We performed ground truthing of the LST dataset by comparing its temperature values to in situ temperature measurements from the USGS Pilot Station gauge (Figure 3). We define the offset of the LST as the difference between the LST temperature and the contemporaneous Pilot Station in situ temperature. We find LST is very accurate compared to in situ measurements (Figure 3b). Both the mean and median offset of the LST dataset are 0.45°C with a standard deviation of 1.89°C . There are two substantial outliers in this data set with offsets of 6.2°C and 8.7°C . One outlier is caused by optically thin clouds that we were unable to effectively mask out, and the cause of the other is unclear. Excluding these outlier points, the mean offset becomes 0.73°C with a median of 0.46°C and a standard deviation of 1.17°C . We will use these values for this study. The absolute values of these offsets are very similar to those calculated by Baughman and Conaway (2021), who found a mean difference of 0.47°C . However, they found a negative bias in the LST data (i.e., LST values tend to be colder than the in situ values), whereas we find a positive bias. This is likely due to a combination of small differences in method of temperature comparison such as the boundaries of the region of interest and our incorporation of several more years of data, including Landsat 9. We note that these offsets are substantially smaller than typical values given by the accompanying LST uncertainty estimate (ST_QA band), which is calculated from atmospheric correction uncertainties and distance of a pixel to the nearest cloud.

The source of the small offset residual is unclear, but Hulley et al., (2012) have found that the largest source of error in the calculation of LST is air humidity, which affects the atmospheric correction. This variable is approximately constant across the

short stretches of river considered here, so the accuracy of the relative temperature within an image is higher than the accuracy of the absolute temperature.

We do not expect water turbidity to be a source of systematic error in the LST measurements (Wen-Yao et al., 1987; Wei et al., 2017). While turbidity can affect water's emissivity and therefore the calculation of temperature from thermal emission measurements, Wen-Yao et al. (1987) found that significant deviations in water emissivity only begin to occur at sediment concentrations of 10^4 – 10^5 mg/L, and the largest turbidity found in Alaskan rivers is around 1000 mg/L (Chikita et al., 2002) and is usually much less than that (Brabets and Ourso, 2013). Similarly, Wei et al. (2017) model the effects of turbidity on emissivity for application to remote sensing of sea surface temperature, and they found that turbidity has a negligible effect (0.2°C) for sediment concentrations smaller than 1000 mg/L. We corroborated this finding by comparing the temperature difference between in situ and remotely sensed temperature to the near-infrared albedo ($0.85 - 0.88 \mu\text{m}$), which acts as a proxy for turbidity (e.g. Wu et al., 2014; Hossain et al., 2021). We show the results of that comparison in Figure 3c, excluding the two large negative outliers in Figure 3b. We find no correlation between these variables, including the absence of the U-shape that would be expected if higher turbidity led to an increase in the absolute value of the error.

Finally, ground truthing remotely sensed temperature data for lakes and oceans must contend with the skin-to-bulk temperature effect, in addition to the larger scale thermal stratification that is often present in poorly mixed water. That is, Landsat and other remote sensing temperature detectors measure the temperature of the top ~ 10 cm of the water, which is influenced by evaporative cooling compared to the bulk temperature beneath the surface (Schluessel et al., 1990; Minnett et al., 2011; Wilson et al., 2013; Javaheri et al., 2016). Because of this evaporative cooling effect, the skin temperature is typically lower than the bulk temperature by $<0.5^\circ\text{C}$ (Schluessel et al., 1990). This effect is likely present in our data for Arctic thaw and oxbow lakes. However, disturbances to the surface such as waves are known to decrease the skin temperature effect (Donlon et al., 2002), so while there is an absence of studies on these skin temperature effect for

ivers, because rivers are fully turbulent, it likely has a negligible effect on inferring bulk river temperature from the surface (Torgersen et al., 2001).

In summary, we are confident in the ability to use this dataset to identify spatially coherent patterns in the bulk river temperature without correction. The small temperature misfits between our data and in situ gauges are substantially smaller than the spatial and temporal patterns in temperature we analyze. Data shown for lakes, on the other hand, may reflect only surface temperatures modified by skin temperature effects.

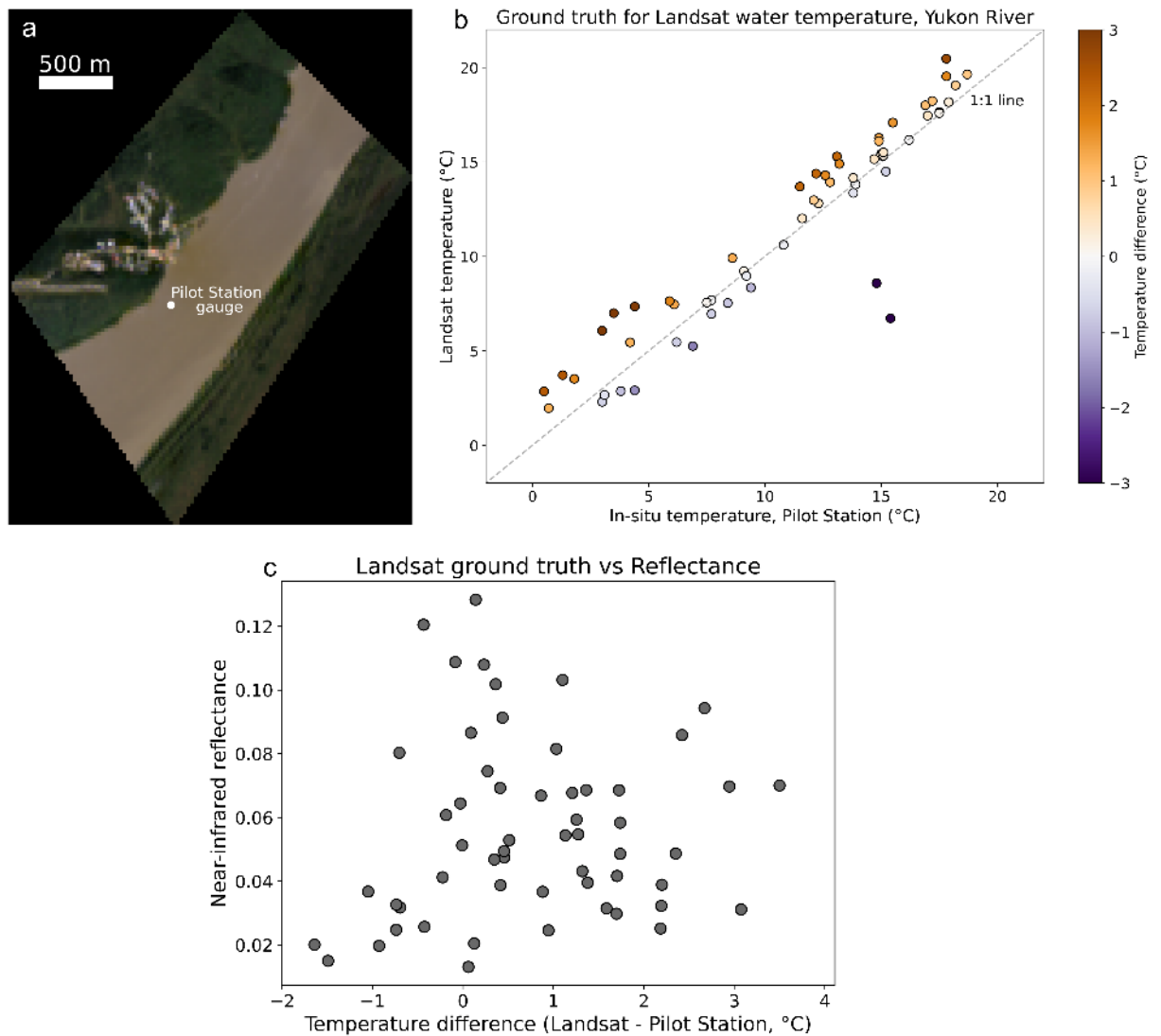


Figure 3: a) The location of the USGS temperature gauge at Pilot Station, station number 15565447, on the Yukon River. The basemap is an RGB image from Landsat 9, and the borders of the image show the region of interest around the gauge delineated for this ground truthing. b) Comparison of temperatures measured in situ by the gauge at Pilot Station to temperatures extracted from the LST calculated from Landsat thermal emission measurements. Each point represents the mean water temperature from one LST image surrounding the gauge location and the contemporaneous gauge temperature and is colored by the difference in value of LST temperature versus in situ temperature. The 1:1 line is plotted for reference. c) The temperature difference between the LST temperature and the in situ temperature vs. the near-infrared reflectance, a proxy for turbidity. Here we have excluded the two large negative outliers $< -5^{\circ}\text{C}$ shown in Figure 3b. No correlation is seen between the LST error and turbidity.

3.2 The Koyukuk River

Using the LST dataset and our water-masking and processing workflow, we generated temperature maps of the meandering stretch of the Koyukuk River near Huslia. We examined spatial patterns in these temperature maps as well as placing these patterns in context of in situ data. The Koyukuk is a major tributary of the Yukon River and allows us to examine patterns in the surface temperature of a meandering, migrating river with several oxbow lakes, including those that are both fully and partially connected to the river, and numerous thermokarst lakes. Figures 4a and b show the Huslia air temperature and Yukon River discharge at the three times we examined compared to typical seasonal values. The air temperature values of the selected dates fluctuate within typical values (Figure 4a). The discharge on the Yukon River at these times are higher than the mean, including outside of one standard deviation for the summer date of 8/30/2016 (Figure 4b).

The water temperature maps demonstrate the surface water temperature varying seasonally and spatially across this meandering riverine corridor. Over the course of an unfrozen season (though as represented by three different years), the Koyukuk's temperature changes from $0\text{--}15^{\circ}\text{C}$ (Figure 4c–e). In the spring, the river is approximately 3°C colder than the air temperature; in the summer, they are almost identical (14°C); and in the fall, the river is 4°C warmer than the air (Figure 4a, c–e). This stretch of the

Koyukuk River is surrounded by dozens of small thermokarst lakes that range in size from $>900 \text{ m}^2$ —the minimum resolvable by Landsat imagery—to approximately 8.5 km^2 (Figure 4c–h). As our data demonstrate, over the course of a season the relative temperatures between the Koyukuk River and these thermokarst lakes change. In the spring and summer, the river is colder than the surfaces of most of the lakes; the difference in temperature is around 5°C in the spring and 2°C in the summer (Figure 4f, g). In the fall, that trend reverses, with the Koyukuk River being 3°C warmer than the surrounding thermokarst lakes (Figure 4h). Figures 4c–h demonstrate that the main channel of the Koyukuk is thermally homogenous at the resolution of the available data. This reflects the thorough mixing of the river as expected for a turbulent water body.

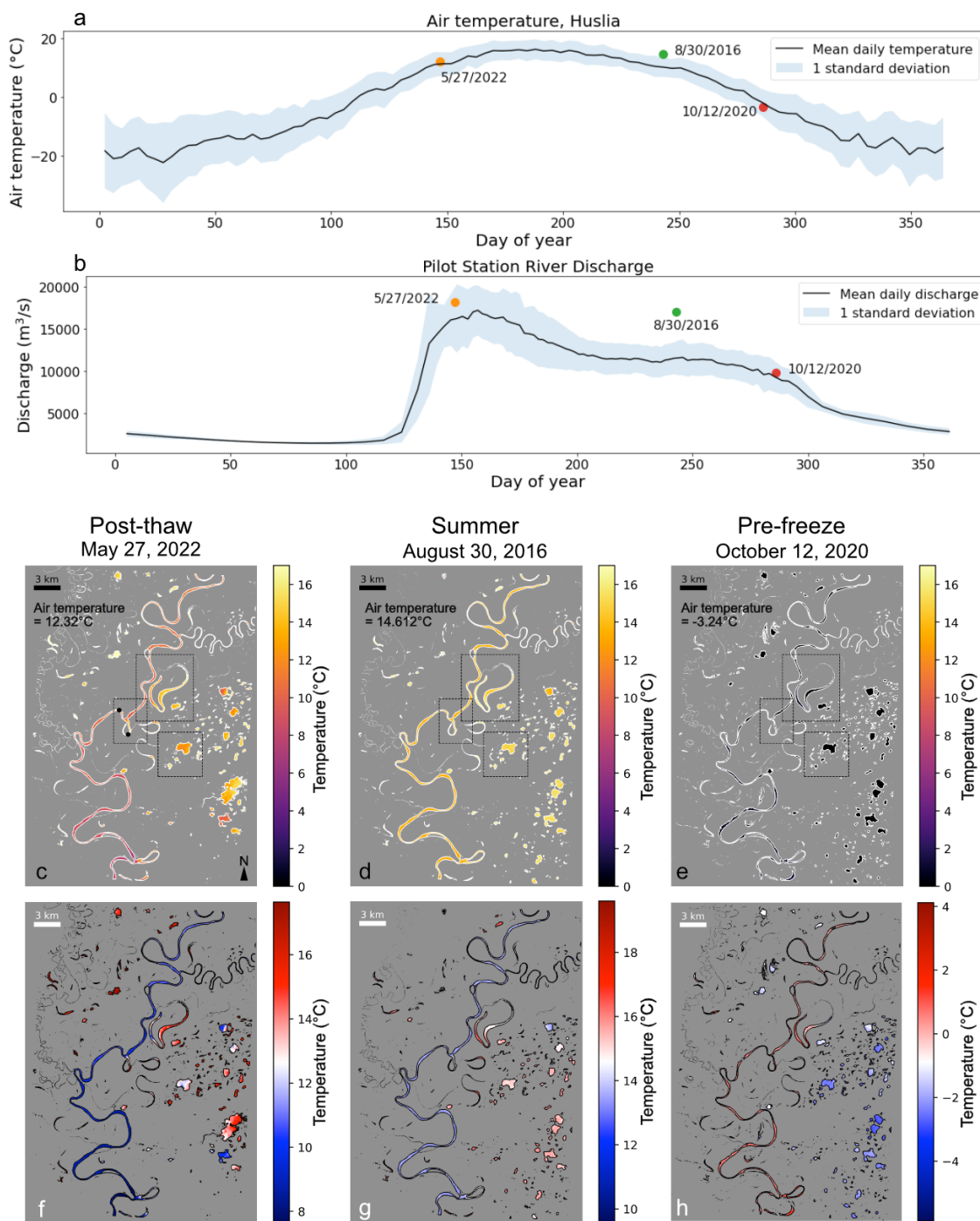


Figure 4: In situ and Landsat data for Huslia on the Koyukuk River. a) In situ mean daily air temperature from 1994–2024 measured by the near-surface temperature sensor at Huslia Airport. b) Mean daily river discharge from 1991–2024 measured by USGS’s Pilot Station of the Yukon River. c–e) Processed Landsat water temperature maps of this

region across the unfrozen season. The color scale is consistent across these images from 0–17°C, demonstrating relative seasonal changes. The boxes indicate locations of detailed observations in Figure 5. The black dots in c mark the locations of the in situ HOBO loggers discussed in section 3.1.2. Labeled air temperature measurements correspond to the points in Figure 4a. f-h) Water temperature maps of this region across the unfrozen season with white on the colorbar set at the mean water temperature in the scene. For each, the color scale is $\pm 5^\circ\text{C}$ from the mean. These maps are centered at 65.76°N, -156.36°E. Flow is from north to south.

Our analysis also shows significant temperature variations between the main river channel, oxbow lakes, and adjacent thermokarst lakes that appear to demonstrate their diverse hydrologic processes and water sources. At a given time, the surface temperature of thermokarst lakes across this small area can vary by several degrees (Figure 4f–h). It is particularly evident in the spring, where the temperature of the larger lake, shown in Figure 5a, is approximately 3°C colder on average than the adjacent smaller lakes. Additionally, Figure 5a demonstrates substantial springtime thermal heterogeneity within the larger lake. The surface temperature of the lake at this time ranges from 11.3–14.7°C, a span of 3.4°C. These patterns are not repeated in the summer or fall. Later in the unfrozen season, there are still temperature variations within and between some lakes (Figure 4g, h), but the heterogeneity is smaller within the lakes shown in Figure 5a–c. In the summer and fall, the temperature variation both within and between lakes is on the order of $<1^\circ\text{C}$ and may reflect small variations in surface temperature but is likely indistinguishable from the noise of the dataset (Figure 5b, c).

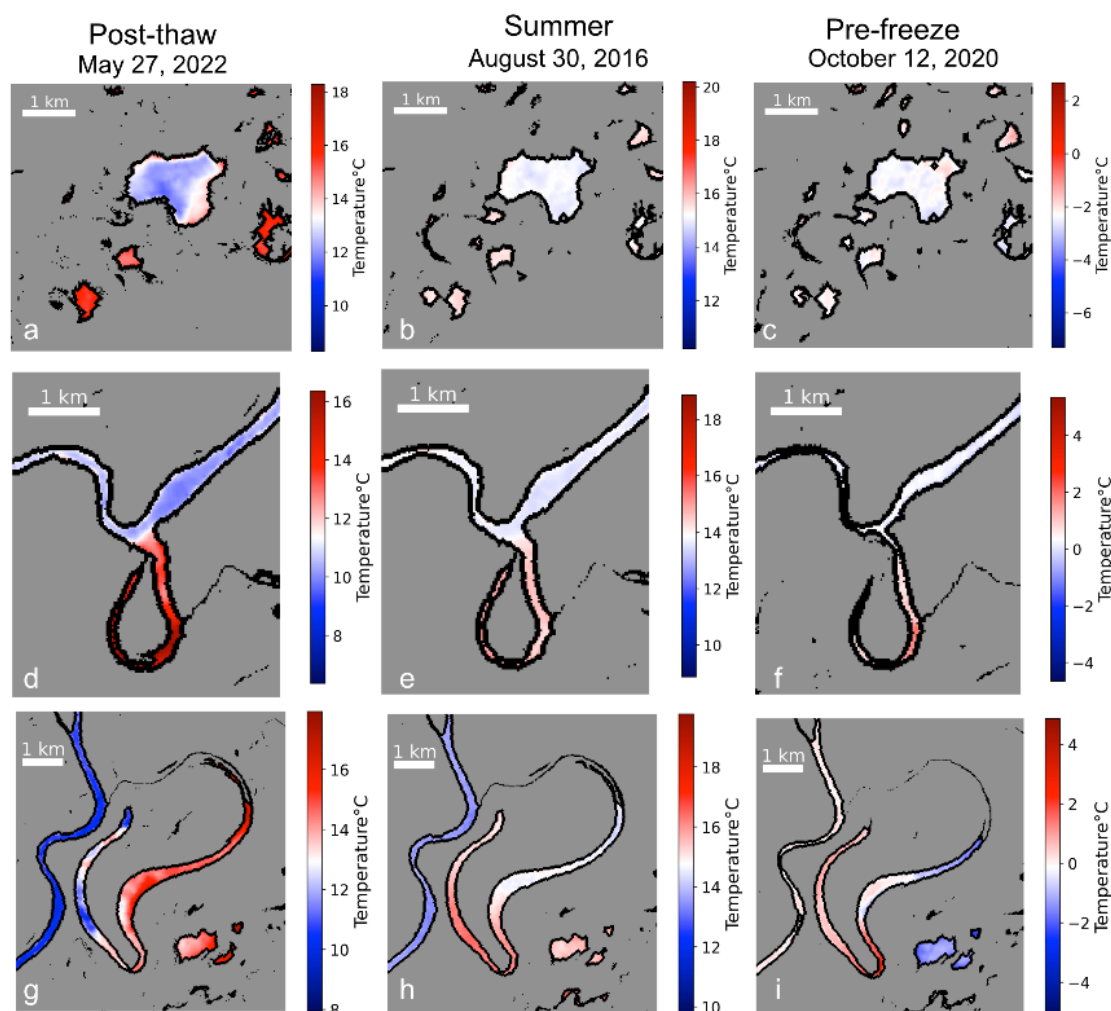


Figure 5: Landsat water temperature maps of locations of interest from the Huslia study site. Temperature colorbars on all maps are set with white at the mean water temperature in the visible extent. a–c) Thermokarst lakes adjacent to the river. d–f) Connected oxbow lake on the main channel of the Koyukuk River. g–i) Sinuous, partially connected oxbow lake on the main channel of the Koyukuk River with significant intra-lake temperature variations.

The temperature maps of the oxbow lake connected to the meandering main channel demonstrate large temperature differences between the lake and the river channel (Figure 5d–f). In all seasons, the Koyukuk River is colder than the surface of the oxbow lake. This generates a temperature gradient across the lake from coldest where the water mixes with the river at the channel connection to warmest most distally. Because this

oxbow lake forms a closed loop that is connected to the river channel at one point on both sides, this creates a divergent temperature pattern (the discharge in the fall is low enough that the western side of the lake appears disconnected, but examination of the mNDWI map shows that the western connection remains below the level of detection of the water mask). The magnitude of that gradient varies across season from 5°C in the spring (Figure 5d) to 2°C in the summer (Figure 5e), to 1°C in the fall (Figure 5f).

A close examination of a long, sinuous oxbow lake partially connected to the Koyukuk River reveals an anomalous temperature pattern (Figure 5f–i). It is similar to the temperature pattern seen in the fully connected oxbow lake in Figure 5d–f, but in this case the sinuous oxbow lake is primarily connected to the main channel on the upstream side. Though it was not detected by the water mask, examination of color variation in the visible RGB images indicates that there is a thin <30 m wide stream connecting the downstream side of this oxbow lake to the Koyukuk River in the spring and summer, across which there may be some but likely minimal mixing. In the fall, the lake appears fully disconnected on the downstream side.

In all seasons, our data show that there are substantial ($>3^{\circ}\text{C}$) temperature variations across the surface of this ~20 km-long oxbow lake. The temperature pattern appears similar in the summer and fall, with the warmest temperatures found near the bend most distant from the river channel and colder temperatures on either side (Figure 5h, i). In the spring, the oxbow lake has the warmest temperatures on the upstream leg of the lake and varying patches of colder and warmer water on the downstream leg (Figure 5g). The visible image of this lake reveals that the summer temperature patterns closely follow the color of the surface water, with the lighter/brown colors indicating more turbid water and the darker/green colors indicating less turbid water, as shown in Figure 6. Turbidity should not substantially affect Landsat's measurement of the surface temperature, as discussed in Section 3.1, so the corresponding patterns of these parameters suggest that both temperature and turbidity are demonstrating the hydraulics of the lake and river mixing.

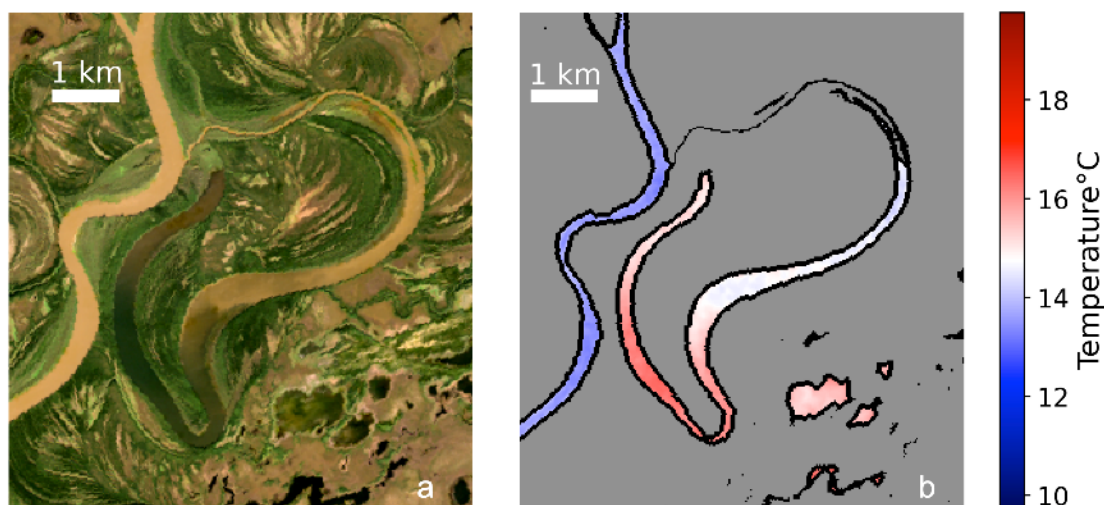


Figure 6: a) Enhanced visible RGB image of the sinuous oxbow lake on the Koyukuk River taken on August 30, 2016. b) Detailed view of Figure 5h, showing the same date as 6a. The color scale is set with white at the mean water temperature in the visible extent.

3.2.1 Comparing surface temperature to temperature at depth

We also compared the surface water temperature as measured with the LST dataset to the in situ water temperature several meters below the surface. Over the 2023 unfrozen season, in situ water temperature data were collected continuously using HOBO temperature loggers at several sites on the Koyukuk River near Huslia. These loggers were anchored a few centimeters above the riverbed, so the depth varied with the river stage. The in situ temperature was consistently measured every 15 minutes, from which we calculated the daily mean temperature for each logger. We compared the surface and deep temperatures for two locations indicated in Figure 4c: an oxbow lake (Figure 5d–f) and within the main Koyukuk channel 5 km downstream of the oxbow lake (Figure 4c). We compared these values to the mean instantaneous surface temperature of a small cloud-free area extracted from Landsat images taken on the same day around the location of the logger. We were limited to <10 data points from each location due to cloud cover. For each, we plotted a linear regression of the difference in temperature between the

surface and at depth versus the date and versus the water depth recorded by the logger (Figure 7).

For the main channel, the temperature differences between the surface and depth (13–18 m) are small. In many cases, the surface and deep temperatures are essentially equal (within the uncertainty of the absolute accuracy of the remotely sensed and in situ temperature measurements) (Figure 7a–c). The remotely sensed surface values tend to be slightly higher than the deep temperatures where there are small differences, which may be in part due to the small positive bias in the remote sensing measurements. There is a substantial difference between the surface and deep temperature on August 10, and it is unclear why, but must be related to a transient and local cold water plume. Excluding the one outlier, there appears to be no systematic correlation between surface versus deep temperature difference with day during the summer (Figure 7b) nor with depth of the river (Figure 7c). This is indicated by the low slopes of their respective linear regression fits (fit without the outlier). We interpret that this indicates the expected turbulent mixing of the river.

For the oxbow lake, the surface temperatures are consistently higher than the temperatures measured at depth (10.15–15.43 m). Temperature differences between the surface and at depth range from 0.37 to 6.38 °C (Figure 7d). There does not appear to be a correlation between the temperature difference and the date, as indicated by the low regression slope and r^2 value. There is positive correlation between the temperature difference and the depth of the logger, with smaller temperature differences for days where the logger depth was smaller. The slope fit to this relationship for the oxbow lake is an order of magnitude greater than that for the channel (Figure 7c, f). We interpret these observations as demonstrating the thermal stratification of this oxbow lake. This stratification was somewhat more pronounced when the lake was deeper, showing a larger thermal gradient (Figure 7f). There appears to be little correlation between date and thermal stratification (Figure 7e). These data were taken from June to August, which likely represents a similar thermal regime, as data collection begins after complete ice melting and ends well before the initiation of re-freezing.

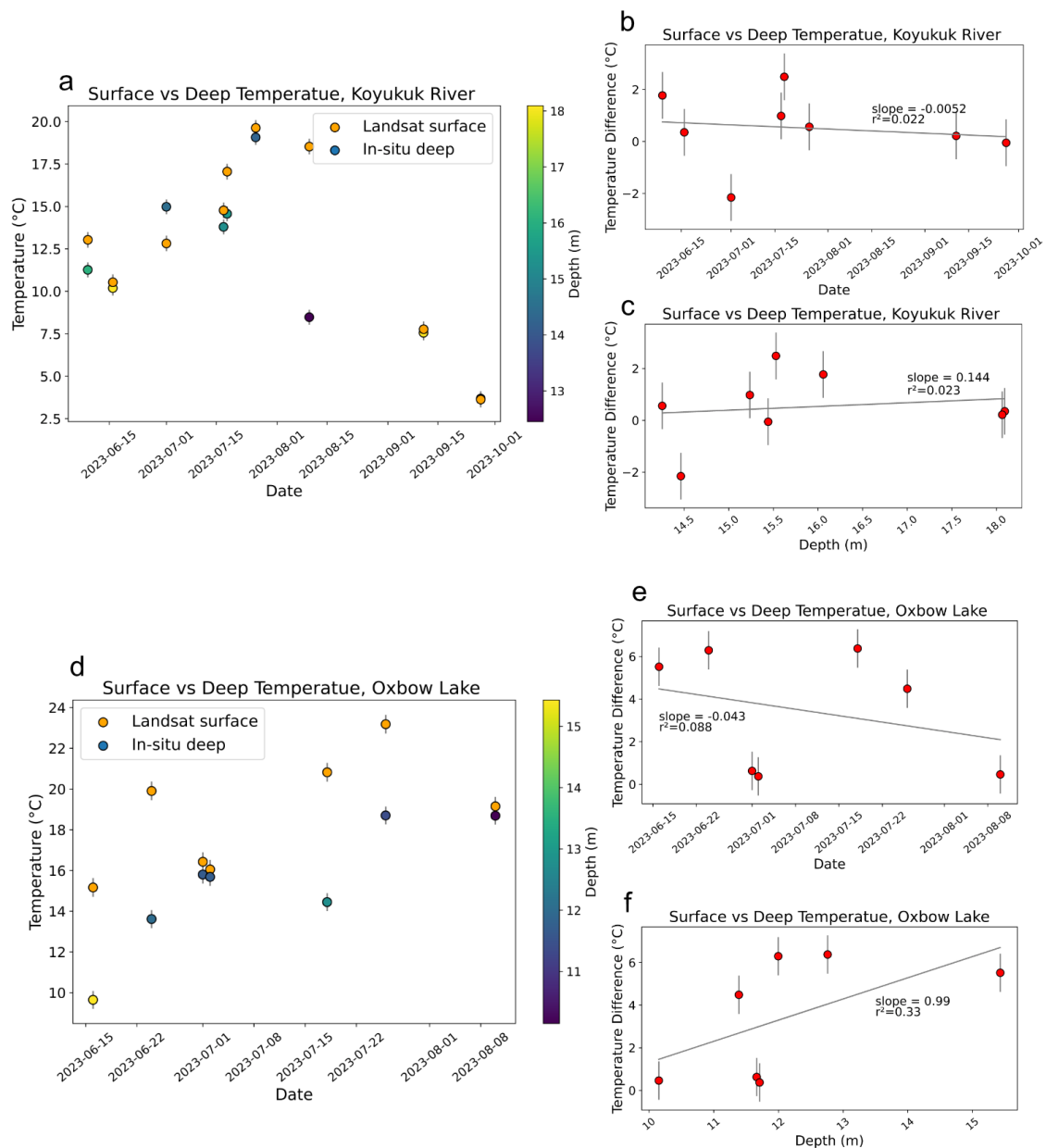


Figure 7: A comparison of surface water temperature extracted from the LST to in situ measurements taken at depth by HOBO loggers. The error bars on the Landsat measurements are $\pm 0.46^\circ\text{C}$, the mean error of the LST dataset compared to the Pilot Station in situ temperatures. a–c) Surface temperature vs. temperature at depth on the main channel of the Koyukuk River. Trendlines plotted in (b) and (c) were calculated without the large outlier temperature value recorded in August by the in situ logger. d–f) Surface temperature vs. temperature at depth for the distal portion of the oxbow lake examined in detail in Figure 5d–f.

3.3 The Yukon-Tanana River confluence at Tanana town

We next examine patterns of surface water temperature at the confluence of the Yukon and Tanana Rivers. At the point of confluence, both rivers are anastomosing. The Yukon flowing dominantly northeast–southwest, and the Tanana flows southeast–northwest before both join into the westward-flowing Yukon River. We focus on examining the contemporaneous relative temperatures of these two rivers as well as the thermal structure of the Yukon downstream of the confluence. Remote sensing provides the unique opportunity to gain a comprehensive view of the spatial distribution of temperature and length of mixing in such a confluence. Figures 8a and b indicate the air temperature at this confluence (Tanana town) and the downstream Yukon River discharge at the three dates we examined compared to typical seasonal values. The air temperature on the post-thaw date of 5/19/2021 is slightly higher than one standard deviation from the mean of this date, but all other temperature and discharge values are within the one standard deviation envelope.

We first compare the temperature of the river water to that of the air. The three dates examined here show that Yukon and Tanana River temperatures vary from approximately 3–14°C over the unfrozen season (Figure 8c–e). Like the Koyukuk River (Figure 4), these rivers are colder than the air temperature in the spring by up to 7°C, nearly identical in the summer (~15°C), and warmer than the air temperature in the fall by 5°C (Figure 8a, c–e).

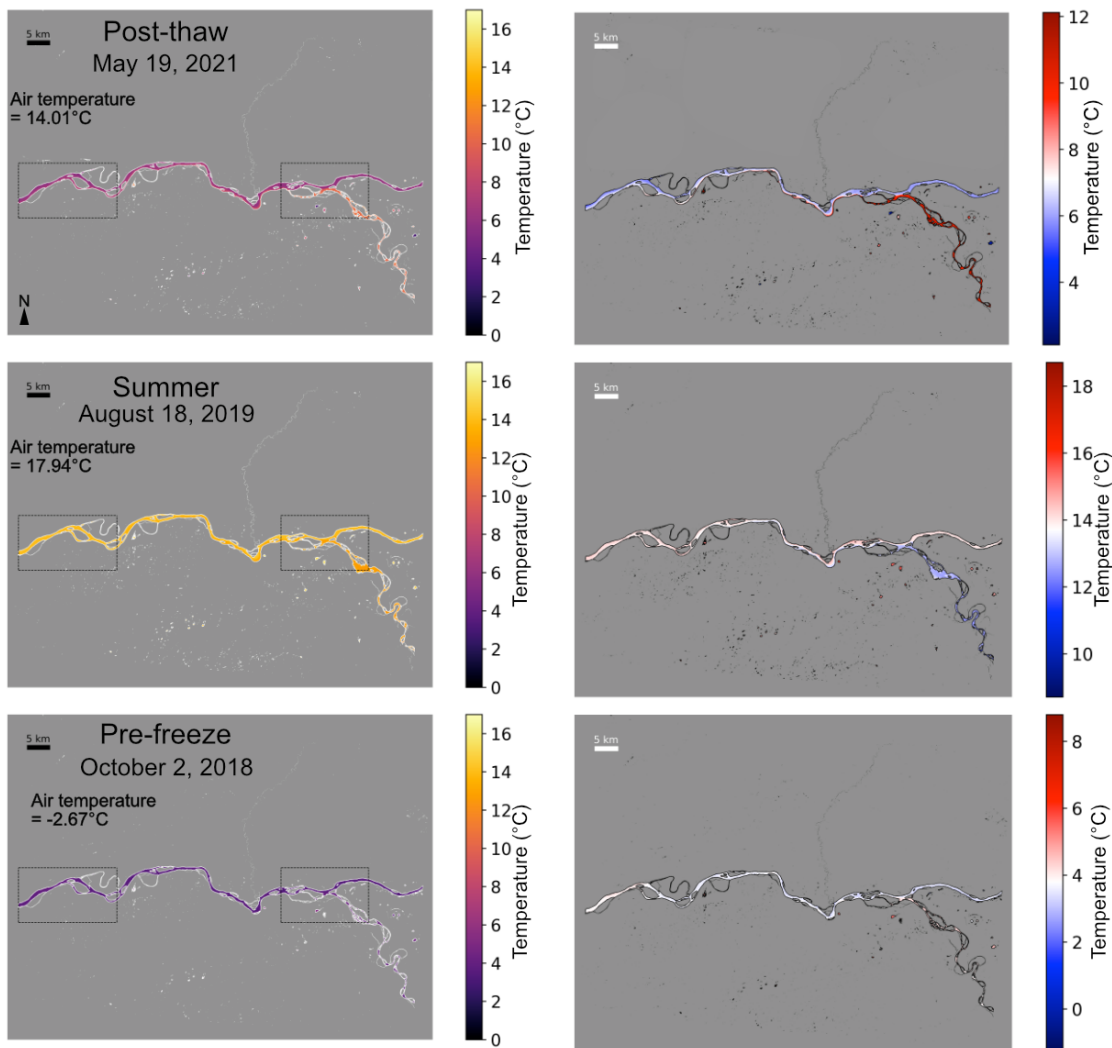
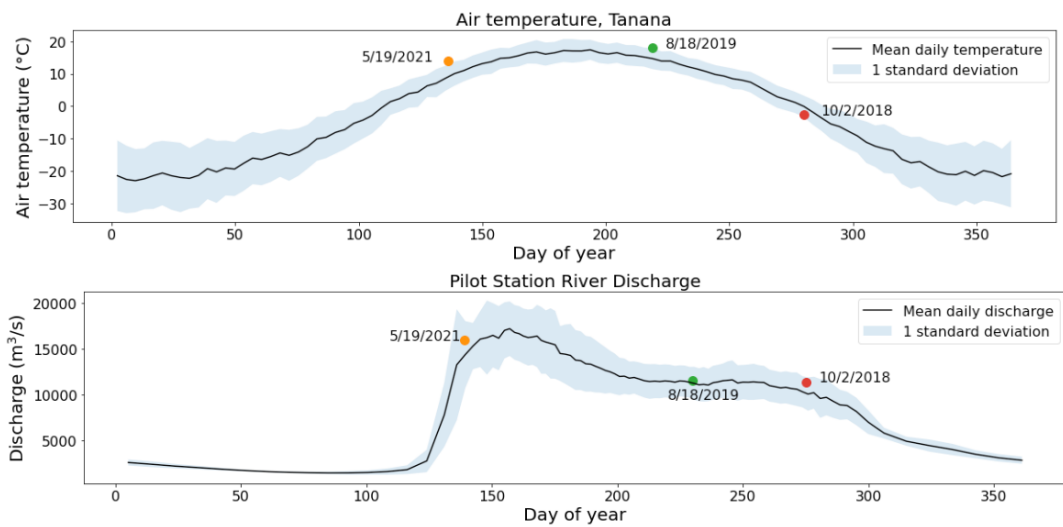


Figure 8: Data for Tanana town at the confluence of the Yukon and Tanana rivers. a) Mean daily air temperature from 1943–2024 present measured by the near-surface temperature sensor at Ralph M Calhoun Memorial Airport. b) Mean daily river discharge from 1991–2024 measured by USGS’s Pilot Station of the Yukon River. c–e) Landsat water temperature maps of this region across the unfrozen season. The color scale is consistent across these images from 0–17°C, demonstrating relative seasonal changes. The boxes indicate locations of detailed observations in Figure 9. Labeled air temperature measurements correspond to the points in Figure 8a. f–h) Water temperature maps of this region across the unfrozen season with white on the colorbar set at the mean water temperature in the scene. For each, the color scale is $\pm 5^\circ\text{C}$ from the mean. These maps are centered at 65.18°N, -152.63°E. Flow is from right to left.

We focus on comparing the relative temperatures of the two rivers at the point of intersection (Figure 9a–c) and 100 km downstream from the confluence (Figure 9d–f). As expected, each river individually is largely thermally homogenous before the intersection. Because of the introduction of a new source of water at the confluence, the combined Yukon then becomes thermally heterogenous (Figure 9a–c). Throughout the unfrozen season, the relative temperatures of these two rivers changes. In the spring and fall, the Yukon is colder than the Tanana, by margins of $\sim 5^\circ\text{C}$ and $\sim 1^\circ\text{C}$, respectively (Figure 9a, c). In the summer, the Yukon is $\sim 1.5^\circ\text{C}$ warmer than the Tanana (Figure 9b).

Downstream of the confluence where both rivers merge into the Yukon River, the cross-sectional temperature variation decreases until the two rivers are fully mixed. In the summer and autumn, the rivers have thermally homogenized at a distance of 100 km from the confluence (Figure 9e, f). This is indicated by the lack of detectable lateral thermal gradient across the Yukon on these dates. In the spring, where there is the greatest initial difference in the river temperatures, there is still an apparent temperature gradient of $\sim 2^\circ\text{C}$ across the river 100 km from the confluence (Figure 9d).

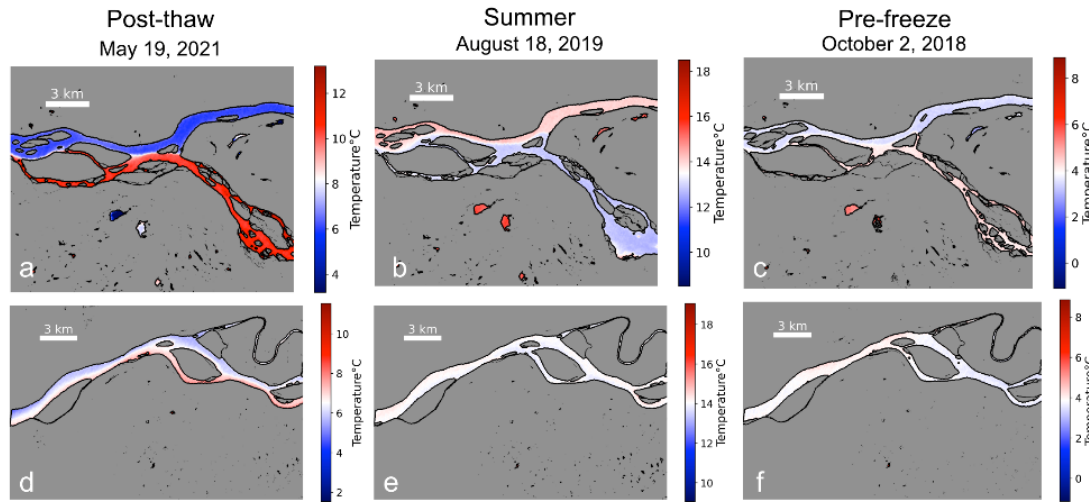


Figure 9: Water temperature maps of locations of interest from the Tanana town study site. Temperature colorbars on all maps are set with white at the mean water temperature in the visible extent. a–c) Initial contact of the confluence between the Yukon River (northern branch) and Tanana River (southern branch). d–f) Stretch of the Yukon River 100 km downstream of the confluence. Flow is from right to left.

We interpret these temperature maps as demonstrating the forces affecting water temperature of these two rivers. The temperature patterns suggest that for rivers in the Arctic, where there are especially large seasonal and latitudinal temperature variations, relative contemporaneous temperatures of the water bodies are set primarily by latitude and secondarily by water source. The Yukon River traverses higher latitudes before the confluence, while the Tanana River flows from lower latitudes. Warmer air temperature arrives earlier to the lower latitudes in the spring, which would increase the temperature of the Tanana River at these lower latitudes relative to the higher-latitude, colder water of the Yukon River. Similarly, warmer air temperatures persist longer into the autumn at the lower latitudes, leading to warmer water temperature in the Tanana River in the autumn. We propose that this process is reflected in the relatively colder temperatures of the Yukon in the spring and autumn (Figure 9a, c). In the summer, air temperature is more consistent across these two watersheds. At this time, the Yukon River is 2°C warmer than the Tanana (Figure 9b). We hypothesize that this is due to the varying contributions of different water sources including snow meltwater, rainwater, and groundwater. At the

confluence, the Yukon has flowed thousands of km from its source of high-elevation glacial lakes, and most of its traverse was across low-elevation terrain. This yields warmer water temperatures. The Tanana is more immediately sourced from meltwater in the Alaska Range mountains, which is consistent with its colder water temperature in the summer. More rigorous modeling would be needed to determine the exact contributions of various water sources and thermal forces on a given river.

Additionally, this site demonstrates how remotely sensed temperature maps can illustrate how temperature acts as a proxy for the mixing of water bodies due to both physical mixing and thermal diffusion. At the point of confluence, the physical separation between the rivers is sharp, as shown by the distinct difference in temperature across the river cross-section (Figure 9a–c). Downstream, the cross-sectional temperature variation decreases until the two rivers are fully mixed. This turbulent mixing length scale is primarily a function of the relative discharges of the two rivers and their miscibility due to differences in density caused by suspended sediment content and temperature (e.g. Kenworthy and Rhoads, 1995; Konsoer and Rhoads, 2014; Pouchoulin et al., 2020). In the summer and autumn, the rivers have fully thermally mixed at a distance of 100 km from the confluence (Figure 9e, f). In the spring, likely due to the greater initial difference in the river temperatures, there is still an apparent temperature gradient across the river 100 km from the confluence (Figure 9d). Remote sensing of turbidity has been used to examine mixing at river confluences (e.g Umar et al., 2018), and our results support that temperature can also be used to track these hydrodynamic processes.

3.4 The Yukon River at Beaver

Lastly, we generate and examine water temperature maps of a stretch of the Yukon River near Beaver. This region represents the typical anastomosing morphology of the Yukon. Figures 10a and b indicate the local air temperature and the downstream Yukon River discharge at the three times we examined compared to typical seasonal values. All temperature and discharge values on the dates examined are within one

standard deviation of their mean values except for the discharge on the pre-freeze date of 10/7/2019, which is slightly lower than typical values.

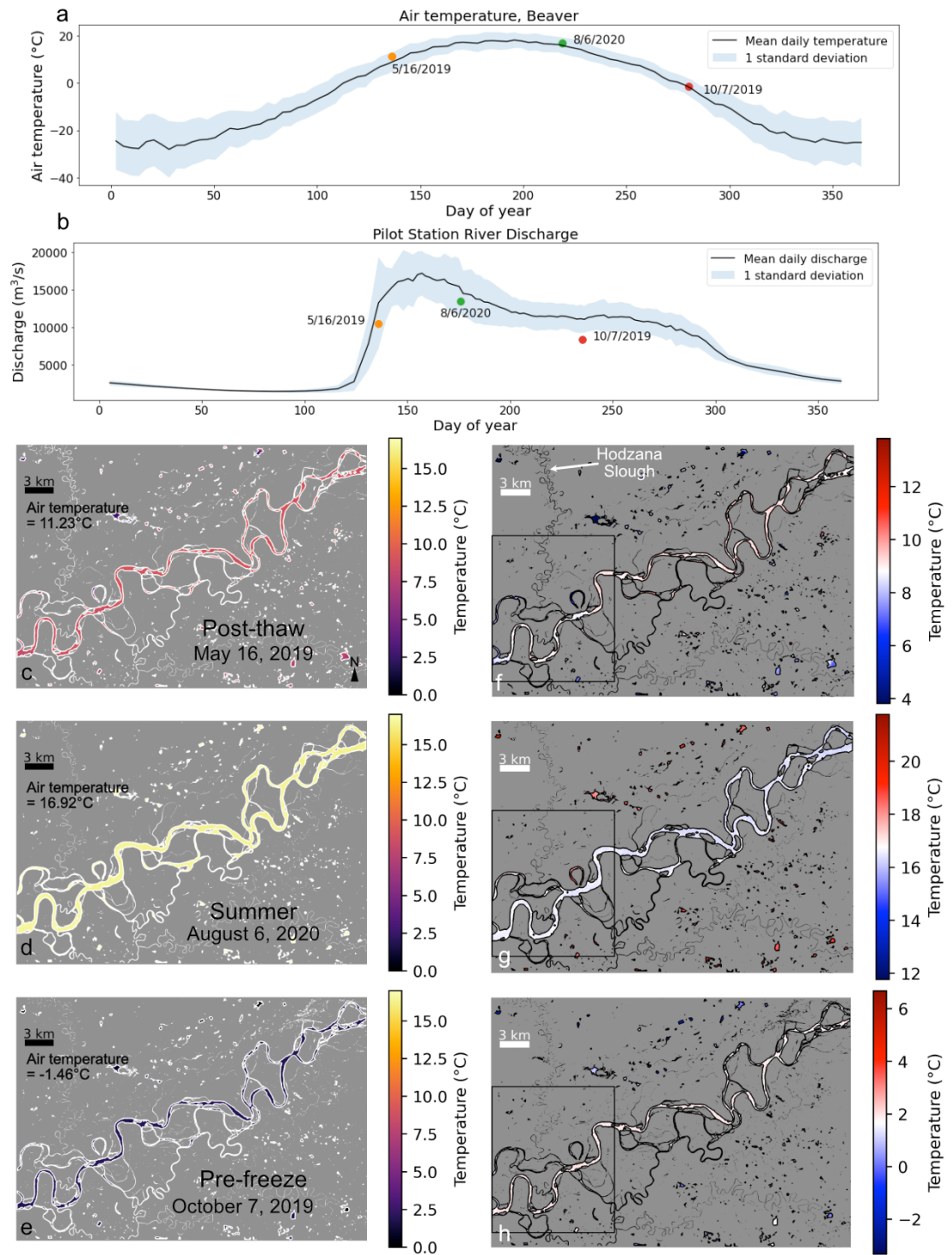


Figure 10: Data for Beaver on the Yukon River. a) Mean daily air temperature from 1948–2024 present measured by the near-surface temperature sensor at Fort Yukon Airport. b) Mean daily river discharge from 1991–2024 measured by USGS’s Pilot Station of the Yukon River. c–e) Water temperature maps of this region across the unfrozen season. The color scale is consistent across these images from 0–17°C, demonstrating relative seasonal changes. The boxes indicate the location of the detailed observation in Figure 11. Labeled air temperature measurements correspond to the points in Figure 10a. f–h) Water temperature maps of this region across the unfrozen season with white on the colorbar set at the mean water temperature in the scene. For each, the color scale is $\pm 5^\circ\text{C}$ from the mean. These maps are centered on 66.345°N, -147.40°E. Flow is from northeast to southwest.

Consistent with the other locations examined, this stretch of the Yukon River is largely thermally homogenous at this resolution. Near Beaver, the Yukon River is anastomosing with a complex geometry composed of numerous river threads and sloughs. Despite these numerous channels, our generated water temperature maps demonstrate that the surface water temperature of the major anastomosing reaches is approximately constant across the whole stretch indicating a high degree of connectivity (Figure 10d–h). Where and when sloughs and secondary channels are wide enough for their temperature to be measured accurately, such as late spring–summer, temperatures also closely match that of wider threads. One deviation from this homogeneity is a slight decrease in temperature on the downstream end of the river in the spring and fall (Figure 11a, c). Temperature decreases after the intersection of the Yukon with the small Hodzana Slough flowing into it from the north. In the summer, there is no detectable decrease in temperature after the confluence (Figure 11b).

Similar to our observations of oxbow lakes in Huslia, the oxbow lake along the Yukon shown in Figure 11 typically differs in temperature from the adjacent river. In the spring, the lake is $\sim 3^\circ\text{C}$ colder than the river; in the summer, the lake is $\sim 2^\circ\text{C}$ warmer than the river; and the temperatures of the two are comparable in the fall. Unlike in Huslia, this oxbow lake is largely or entirely disconnected from the river. Therefore, we do not observe, nor do we expect to observe, a robust relationship between surface water temperature and distance from the river as we did in Huslia (Figure 5d–f). Rather, the oxbow lake near Beaver appears to behave analogously to other floodplain lakes in the

region. We interpret the surface temperature of these lakes to reflect vertical thermal stratification and internal mixing processes as in the other study locations.

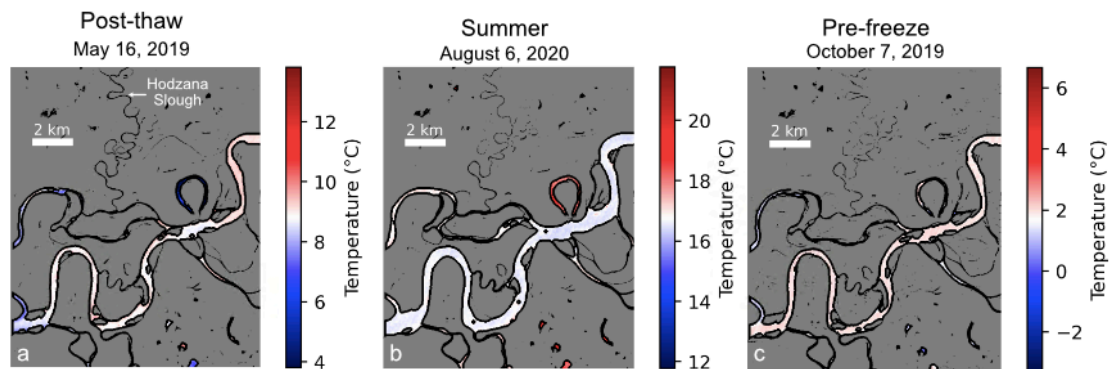


Figure 11: Water temperature maps of a location of interest from the Beaver study site. Temperature colorbars on all maps are set with white at the mean water temperature in the visible extent. a–c) Downstream portion of this short anastomosing stretch of the Yukon River, before and after the intersection with the Hodzana Slough.

4 Discussion

4.1 Vertical temperature structure

By comparing the remotely sensed surface water temperature measured by the LST to in situ temperature measured at depth, we can contrast the vertical temperature structure of Arctic rivers and lakes and identify how remote sensing can be appropriately applied to understand water temperature of river corridors. The expectation is that rivers should be thermally well-mixed vertically because they are fully turbulent (Franca and Brocchini, 2015). This is supported by our comparisons of LST to both the in situ Pilot Station gauge on the Yukon River and the HOBO logger anchored at depth in the Koyukuk River. The similarity of the temperature measured at the surface by LST and at depth by an in situ gauge (Figure 7a) demonstrates that there is no clear thermal stratification of the river channel, and it is well-mixed throughout the vertical profile. This also indicates that rivers either lack an evaporative cooling thermal skin effect as has been theorized (Torgersen et al., 2001), or that if it exists, it is within the LST uncertainty. This result demonstrates the power of remote sensing for applications to measuring and understanding river water

temperature. By measuring the temperature of just the top 10 cm of the water, the LST can accurately capture the temperature of the entire river water column.

Conversely, our results demonstrate that while remote sensing surface temperature can yield valuable information about lake surface temperature, it does not reflect the thermal behavior at depth. This is demonstrated by the difference in the oxbow lake surface water temperature measured by LST and the temperature at depth measured in situ, with higher temperatures at the surface indicative of thermal stratification (Figure 7d). This is expected for lakes of this depth, as lakes >10 m deep typically exhibit steep thermoclines (Gorham and Boyce, 1989; Boehrer and Schultze, 2008; Pöschke et al., 2015; Cannon et al., 2019). Therefore, while remote sensing can be used to accurately measure the water temperature at a lake's surface, for water bodies that can achieve stratification, in situ observations are required to understand the temperature at depth.

4.2 Seasonal patterns in water temperature

Because LST provides high-resolution temporal coverage (repeat observation time is typically 1–7 days), our data demonstrate how surface water temperature within these Arctic riverine corridors evolves seasonally. We find that the dates we examined from post-ice breakup to pre-freezing capture the large swings in water temperature these rivers experience over the course of the unfrozen season. All rivers demonstrate >10°C swings in water temperature over the season, from just above freezing to an average temperature of ~15°C. By comparing the remotely sensed LST temperature values with those of in situ air temperature monitors, we see that this water temperature evolution is similar to the magnitude of the air temperature variation.

Despite the differences in hydrological context of these rivers including elevation, permafrost distribution, and geometry both locally and in their upstream watersheds, the three sites examined here appear to largely track local air temperature well. In all locations, there is a clear offset in water temperature compared to air temperature in the spring and fall of 3–7°C due to water's higher thermal inertia but a close match of water and air temperature (0–4°C) in the summer (Figure 4, 8, 10).

However, within the examples we examine here, we do observe significant deviations from this close correlation of river temperature to air temperature. At the confluence of the Yukon and Tanana Rivers, there is a $\sim 5^{\circ}\text{C}$ difference in water temperature between rivers despite the same local air temperature (Figure 9a). While the temperature of both rivers evolves over the course of the season correlated with air temperature, the water temperature difference between them indicates the additional controls on river temperature besides local air temperature and thermal inertia, which we argue include water source and upstream watershed air temperature.

Lake surface water temperature varies substantially within a river corridor at a given time, and so while all lake temperatures do evolve systematically with air temperature across the unfrozen season, they are more decoupled from the air temperature than rivers are (e.g. Figure 4). The seasonal evolution of lake surfaces appears to be strongly controlled by mixing and stratification processes in addition to larger-scale regional trends in air temperature.

We also compared the water temperature to a relative estimation of the local river discharge, as represented by the discharge measured in situ at Pilot Station on the Yukon River. River discharge also varies seasonally, from its highest values just after ice breakup to a fairly consistent plateau until refreezing (Figure 4b, 8b, 10b). If river water temperature varies with discharge, it is more subtle compared to the strong correlation to air temperature. More data including local discharge measurements would be required to disentangle the effects of discharge on river temperature.

4.3 Spatial patterns in water temperature

By providing complete spatial coverage, it is clear that LST can be used to examine the spatial patterns in surface water temperature across riverine corridors. Our primary observation of river temperature is that—excluding the introduction of a new source of water to the river—water temperature is largely homogenous across the 50–100 km long stretches examined. The surface temperatures of these stretches of the Koyukuk, Yukon, and Tanana rivers appears to vary by $<1^{\circ}\text{C}$, within the uncertainty of the LST

measurements. This consistency in surface temperature is evident across river contexts and morphology including meandering (Koyukuk River) and anastomosing (Yukon River) stretches. Even in locations with complex geometry such as the anastomosing region near Beaver, there is thermal homogeneity across the threads, secondary channels, and sloughs that are large enough to be measured with this method (Figure 9f–h).

However, the spatial coverage provided by remotely sensed imagery captures well where there are deviations from this homogeneity in both connected and disconnected water bodies. In particular, we observe that the introduction of a new source of water can create thermal heterogeneities. This is particularly evident at the confluence of the Yukon and Tanana rivers, where the mixing of these different water sources creates a lateral temperature gradient across the combined Yukon River that can still be detectable even up to 100 km from the point of confluence. The remotely sensed temperatures we generated for this study demonstrate how temperature acts as a proxy for the mixing of water bodies due to both physical mixing of the water masses and thermal diffusion. Remote sensing of turbidity has been used to examine mixing at river confluences (e.g Umar et al., 2018), but these results indicate that temperature alone can also be used to track these hydrodynamic processes. This can be used alongside turbidity to separate the effects of physical mixing and thermal diffusion, and it may be useful to understand tributary mixing even if there is no substantial turbidity difference between the rivers.

Lakes in these Arctic river corridors demonstrate different patterns in spatial distribution of surface water temperature depending on their depth and their connectivity to rivers. In particular, we observe that the surface temperature spatial patterns of connected oxbow lakes are distinct from that of disconnected thermokarst lakes. This is likely a function of both their hydrologic connectivity and size. Arctic lakes exhibit variable mixing processes depending on their size and structure. Deep lakes are typically dimictic, experiencing wind-driven overturn twice a year but stagnation and stratification in the summer (Gorham and Boyce, 1989; Boehrer and Schultze, 2008; Pöschke et al., 2015; Cannon et al., 2019). Lakes that are sufficiently shallow ($< \sim 10$ m) tend to be polymictic, that is, wind can mix the full volume more continuously (Taranu et al., 2010; Pöschke et al., 2015). Our surface temperature maps of the oxbow lake examined near Huslia show a

temperature gradient across its surface that appears to track the mixing of the lake water with the main river channel (Figure 5d–f). This thermal stratification is also illustrated by the comparison of the remotely sensed surface water temperature to the water temperature measured in situ at depth (Figure 7d).

The surface temperature maps of the thermokarst lakes demonstrate the control of mixing and other local processes on these shallow water bodies. We observe that adjacent lakes of similar surface area in Huslia (Figure 4f–h) as well as near Tanana town (Figure 9a–c) and Beaver (Figure 10) can vary in temperature by nearly 5°C. Therefore, the remotely sensed surface temperatures likely demonstrate the effects of additional processes beyond the control of air temperature. These processes likely include discontinuous permafrost distribution or mixing processes, and more detailed data would be required to constrain all processes impacting the surface temperature of these lakes. Our data demonstrate that for an Arctic floodplain environment, where these thermokarst lakes are abundant, remotely-sensed temperature maps capture thermal diversity in lake temperature that would not be captured effectively by sparse in situ point measurements.

4.4 Applications of remotely sensed water temperature to the Arctic

Thermal remote sensing of water temperature has a wide array of potential applications to Arctic environments. The remotely sensed water temperature maps we created demonstrate the variability of contemporaneous water temperature across riverine corridors, seasonal temperature changes, and mixing of water bodies and hydraulic connectivity.

An important application of these maps is providing an understanding of the temperatures experienced by different organisms in the ecosystems in and around these bodies of water. In particular, remote sensing of river temperature in Alaska provides critical information about thermal stresses on salmon, which have declined sharply in recent years (e.g. Jacob et al., 2010; Westley, 2020; Thorstad et al., 2021; Biela et al., 2022). Many studies that attribute salmon decline to rising river temperature rely solely on air temperature data as a proxy for water temperature, but remote sensing can be used to

understand actual water temperatures encountered by salmon on their migration from the ocean upriver to their breeding grounds and catalog potentially life-saving thermal refuges (Bilby, 1984; Ebersole et al., 2003; Torgersen et al., 2012). High-resolution (cm-scale) thermal imaging from airborne platforms has been used to identify smaller thermal refuges on the ~ 1 m scale (e.g. Torgersen et al., 2012; Frechette et al., 2018), but with our data, we are able to identify larger possible refuges without need for the expense of dedicated surveys. In particular, we identify anomalously cold regions of rivers at confluences with tributaries or even small sloughs. For example, at the Yukon-Tanana confluence, the Tanana River brings in water 2–3°C colder than the Yukon that significantly cools the stretch of the river downstream of the confluence (Figure 8), and even the Hodzana Slough significantly cools the river near its intersection with the Yukon River at Beaver (Figure 11).

In permafrost-rich environments such as the Arctic, the remotely sensed water temperature data with high spatial and temporal resolution can be used to help characterize and predict the rate of riverbank erosion, as a relationship has been found between river water temperature and bank erosion rate (Costard et al., 2003; Douglas et al., 2023; Geyman et al., 2024). Because we show that the surface water temperature measured by satellites is a good representation of the water temperature at depth (Figure 7a), our results demonstrate that LST can be used to measure the temperature of the water that is eroding permafrost-bearing banks. For example, we show that the water temperature of the meandering Koyukuk River lags behind the air temperature in the spring after ice breakup (Figure 4), when river discharge is highest and erosion has been found to be substantial (Geyman et al., 2024). In this case, the rate of bank erosion is likely thermally-limited by the cold water's ability to melt the cohesive permafrost. Later in the summer, the water temperature warms rapidly to match or exceed that of the air, but the discharge is comparatively low. This likely creates transport-limited bank erosion, where the water is able to melt the permafrost but does not have the power to transport away the thawed sediment. This is consistent with remote sensing observations of the timing of bank erosion in this region (Geyman et al., 2024) and demonstrates that remote sensing of water

temperature can be used to provide critical constraints on riverbank erosion rates, particularly as permafrost continues to degrade due to climate change.

Additionally, understanding the spatial distribution of surface water temperatures allows for more accurate calculations of geochemical fluxes such as greenhouse gas release from rivers and lakes. Constraining these processes is particularly necessary in the Arctic, where permafrost thaw is driving release of organic carbon (Zandt et al., 2020). Quantifying thermokarst lake temperature is necessary to calculate chemical fluxes such as greenhouse gas release from these water bodies, but we demonstrate that remote sensing cannot be used to measure water temperature at depth. However, we also show that the remotely sensed temperature maps can capture significant ($>5^{\circ}\text{C}$) variations between the surface temperatures of adjacent lakes (e.g. Figure 5, Figure 9a), likely reflect variations in the timing and process of lake overturn and mixing. Measurement of water temperature throughout the water column and at depth requires the placement of sensors, which is a challenging and expensive process, especially in the remote Arctic. Our maps demonstrate that remote sensing can be used to guide those placements, for example by identifying lakes that appear representative of the typical thermal state of lakes in a region or by identifying unusual, thermally anomalous lakes. By capturing the contemporaneous surface water temperature across a floodplain, remote sensing can also be used to help extrapolate from in situ point measurements across the region. This can support robust calculation of greenhouse gas fluxes from this crucial source that is predicted to pose significant impacts on the climate.

Remote sensing like the LST dataset can be combined with state-of-the-art models to both fill in gaps in the remote sensing and in situ gauge datasets as well as to predict future changes to river temperature. For example, Chang et al. (2025) combine atmospheric and climate data from ERA5-Land reanalysis (Muñoz-Sabater et al., 2021) with the AKTEMP collection of gauge temperature data. This succeeds in predicting river temperature well, and future work could construct similar models relying on the LST data as the input to expand coverage further beyond the available gauges in Alaska, such as has been implemented with LST in other locations (e.g. Al-Murib et al., 2019; Murphy et al., 2021). Additionally, future work should take advantage of LST's four decade-long

temporal record, which is longer than most gauge records, in addition to its spatial coverage. This allows analysis of long-term thermal evolution across diverse contexts, including climate change-driven trends (e.g. Santos Fleischmann et al., 2025).

5 Conclusions

Understanding water temperature in Arctic rivers and wetlands is essential for predicting permafrost thaw, river erosion, greenhouse gas emissions, and ecosystem health, yet existing observations from in situ gauges and airborne surveys remain spatially limited and difficult to obtain in this remote region. Here we demonstrate the power of the Landsat Land Surface Temperature (LST) dataset for resolving the spatial and seasonal patterns of surface water temperature across Arctic river corridors and their surrounding wetlands. We find that LST can successfully measure temperatures for water bodies wider than ~210 m, with smaller water bodies affected by mixed land–water thermal signals. For sufficiently large rivers and lakes, comparison with in situ measurements demonstrates that LST is reasonably accurate, with a median error of 0.46°C. Across three distinct Yukon River watershed environments in Alaska, we show that remotely sensed surface temperatures closely represent bulk river temperatures, whereas lakes may experience thermal stratification and skin temperature effects that are not captured by remote sensing alone. Water temperatures largely track seasonal air temperature variations, but with a lag caused by water’s thermal inertia, and exhibit substantial (~15°C) seasonal swings characteristic of high-latitude climates. Spatially continuous temperature maps reveal that river temperatures are generally laterally homogeneous because of turbulent mixing, while temperature contrasts occur primarily at tributary confluences, connected side channels, and oxbow lakes, where temperature acts as a tracer of hydrological connectivity and mixing. Thermokarst lakes across Arctic floodplains also exhibit strong spatial variability in surface temperature, likely reflecting differences in mixing and overturn processes, highlighting the need for spatially resolved thermal observations beyond point measurements. Overall, we demonstrate that remote sensing of surface water temperature provides substantially greater insight into the thermal structure and hydrological

connectivity of Arctic river–wetland systems than is possible from existing gauge networks alone, and that these datasets can help advance understanding of the biological, geological, and biogeochemical processes shaping rapidly changing Arctic environments.

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Open Research

The Landsat visible–near-infrared images and the Landsat Land Surface Temperature data are freely available from the United States Geological Survey/NASA through data portals such as EarthExplorer (<https://earthexplorer.usgs.gov/>). The stream gauge temperature data used in Figure 3 and the stream gauge discharge data used in Figs. 4, 8, and 10 are available from the United States Geological Survey National Water Information System (<https://waterdata.usgs.gov/nwis>). The near-surface air temperature data used in Figs. 4, 8, and 10 are available from the National Weather Service/Federal Aviation Administration/Department of Defense through data portals such as the National Centers for Environmental Information (<https://www.ncei.noaa.gov/access/search/data-search/global-hourly>). The in situ water temperature measurements of the Koyukuk River near Huslia, AK that were used in Figure 7 were taken by our collaborators. These data have been submitted for publication to the NSF Arctic Data Center and will be publicly available as soon as possible.

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Chapter 5

SUMMARY, IMPLICATIONS, AND OUTSTANDING QUESTIONS

In this work, we have demonstrated how the powerful tool of satellite-based remote sensing can be used to gain great insight into the processes that have shaped the surfaces of our planet and beyond. We use satellites to understand the record of water on Mars that existed ~3.7 billion years ago, or, with a small shift in the examined wavelengths, to understand the temperature of water that is present on the surface of Earth today. These projects have wide-ranging implications. In Chapters 2 and 3, our results provide further insight into the nature of Mars' chemical weathering history including the duration of water, pH, redox state, and protolith composition. In Chapter 4, our results demonstrate the efficacy of applying remote sensing to understand the spatial and seasonal patterns of river and wetlands water temperature in permafrost-rich environments like Alaska. In both applications, we use light transmitted to distant satellites to learn more about our Solar System.

5.1 Chapters 2 and 3

Since their initial detection on Mars in 2005 (Poulet et al., 2005), Al-phylosilicates have been viewed as a window to understanding Mars' aqueous past. In Chapter 2, we examine the formation of Al-phylosilicate in Mars' Nili Fossae region in light of the continued collection of CRISM and HiRISE imagery and the detection of associated jarosite (Ehlmann et al., 2009; Ehlmann and Dundar, 2015). Focusing on the relationships between the Al-phylosilicate, jarosite, and Fe oxide, we found that the Al-phylosilicate mineralogy and stratigraphy in Nili Fossae is not consistent with formation as part of a weathering sequence with Fe/Mg-phylosilicate from basalt, as had been previously thought (Ehlmann et al., 2009). From our observations, we conclude that the Al-phylosilicate in Nili Fossae most likely formed from a distinctly aluminous and sulfur-bearing protolith, most likely a volcanic ash. These observations change our known story

of what happened in this key site for Mars' alteration history. Rather than recording among the most extensive histories of aqueous alteration on Mars, as had been presumed, we suggest that Nili Fossae instead records a combination of local volcanic processes and a history of more limited aqueous alteration. Our conclusions about the nature of Al-phyllsilicate formation in Nili Fossae serve to add to our understanding of the regional complexity of these Al-phyllsilicate bearing regions across Mars.

In Chapter 3, we performed a global survey of the six primary Al-phyllsilicate-bearing regions across Mars to reexamine, compare, and contrast their stratigraphy and formation processes with an eye towards understanding its localized complexity. We conclude that the Al-phyllsilicate-bearing regions across Mars are consistent with two distinct formation processes. In Hellas Planitia and the Eridania Basin region of Terra Sirenum, the Al-phyllsilicate indeed appears to be consistent with formation from pedogenic leaching of a basaltic protolith. In contrast, in Nili Fossae, Libya Montes, eastern Terra Sirenum, and Valles Marineris, we find that the mineralogy and stratigraphy of the Al-phyllsilicate is more consistent with formation from a volcanoclastic deposit like an ash. We observe jarosite only mixed with Al-phyllsilicate, never with Fe/Mg-phyllsilicate, which we argue indicates jarosite forming in the presence of locally sourced, likely volcanically derived, sulfur. Mawrth Vallis, we determine, has a mix of features consistent with pedogenic leaching and volcanic ash alteration and may represent a region shaped by both processes.

Our results have significant implications for our understanding of Mars' aqueous alteration as well as its volcanism. The formation of Al-phyllsilicate from basalt requires an extensive amount of water, likely an upper limit of tens of millions of years to form the thickest units observed (Bishop et al., 2018). However, because ashes weather far more readily to Al-phyllsilicate, we estimate that an order of magnitude less cumulative duration of water is required to produce much of the observed Al-phyllsilicate across Mars. Additionally, our conclusion that much of the Al-phyllsilicate formed from a volcanic ash suggests a more extensive record of explosive

(ash-producing) volcanism than previously thought. We propose that much of the Al-phyllsilicate acts as a tracer for the extent of explosive volcanism, beyond what poorly preserved physical or structural evidence could indicate. We also conclude that this ash was likely generated from a more evolved, less basaltic volcanism. While Mars is dominantly basaltic (McSween, 2009), this and other evidence for localized evolved compositions (e.g. Christensen et al., 2005; Wray et al., 2013; Rogers and Farrand, 2022; Phillips et al., 2022) suggests the influence of fractional crystallization processes in Mars's interior and demonstrates that more felsic compositions may not be unique to planets with plate tectonics.

While regional studies of Al-phyllsilicate, including our Chapter 2, identify diversity in its formation, global-scale analyses largely lump the Al-phyllsilicate into one consistent formation story, one that requires an extensive amount of water. Where this mineral is found, it is often interpreted to indicate extensive alteration from a basalt or otherwise mafic protolith (e.g. Carter et al., 2015; Moore et al., 2025; Broz et al., 2025). While that may indeed be accurate in some cases, it is likely not the case globally. We conclude that Al-phyllsilicate on Mars should not be automatically synonymous with the highest levels of aqueous alteration, but instead interpretation of its formation process should be grounded in the geology of the region where it occurs, and we have identified which processes dominate in Mars' most significant Al-phyllsilicate-bearing regions.

Our results on the nature of Al-phyllsilicate formation on Mars in Chapter 2 and Chapter 3 prompt several questions for future analysis. In our work, we show that the extensive pedogenic leaching of basalt that had previously been thought to have occurred globally was instead likely isolated to a few key regions: Hellas Planitia, Eridania Basin, and Mawrth Vallis. Of the exposed surfaces of Mars, these three regions may represent the terrain that is the most altered by low-temperature aqueous alteration. The nature of Mars' ancient climate and the amount of liquid water it would need to have supported in the late Noachian–early Hesperian is a subject of continual debate. These extensively altered regions we identified provide valuable constraints on the extent and duration of

liquid water that must have existed in Mars' past. Future work should examine the geologic context of these three sites to understand why they are so altered. What was the nature of water's interaction with them? Were similar processes active in all three regions, and if so, why in those specific locations? Understanding the behavior of water in the regions of Mars perhaps most chemically impacted by its presence will clarify the extent and duration of liquid water that Mars' ancient climate must have supported.

Additionally, in the regions of Mars where we concluded that volcanic ash deposits were the Al-phylosilicate protolith, we often find jarosite in association with the Al-phylosilicate. In Chapter 2 and 3, we conclude that this jarosite likely formed from a contemporaneous or later stage of fluid interaction that leached iron from the surrounding rock and reacted with local ash-sourced sulfur. Future work should look to differentiate between a groundwater and a surface water source for that later stage of fluid, including a detailed examination of jarosite's positioning relative to local topography. Distinguishing between groundwater and surface water processes expands our understanding of the nature of Mars' water at the transition from the predominantly wetter Noachian to the predominantly drier Hesperian period.

While our results demonstrate the power of remote sensing to address in detail questions about Mars' chemical weathering history by relating its composition to its stratigraphy and geomorphic context, we also recognize where the resolution of orbital data is insufficient to fully address these questions. Everywhere we have sent landed missions on Mars has revealed complexity far beyond what can be seen from even the highest-resolution satellite imagery including unexpected stratigraphic relationships and minerals. Therefore, we argue that our results and those of other remote sensing studies support the need for further rover-based observations of Mars. The European Space Agency's ExoMars mission is planned to land in 2030 in Oxia Planum, which likely has laterally continuous phyllosilicates from Mawrth Vallis (Quantin-Nataf et al., 2021; Auré et al., 2026), and may provide our first chance to see these ancient phyllosilicates units up close. Additionally, the return of Al-phylosilicate samples to Earth for laboratory

analysis would be a tremendous boon to verifying their formation mechanism and gaining great insight into Mars' aqueous history. The Perseverance rover may have the opportunity to sample the kaolinite that is observed in Jezero Crater's rim for return to Earth. I argue that such sampling and sample return more broadly should be a priority.

5.2 Chapter 4

River water temperature plays a significant role in almost every process of interest to scientists and the communities that rely on them, but in situ measurements even on Earth are limited, particularly in the Arctic. In Chapter 4, we use remote sensing from Landsat satellites (LST) to generate water temperature maps of three diverse riverine environments in the Yukon River watershed of Alaska, examine the patterns that emerge from these maps, and compare these results to in situ data where available. We conclude that for sufficiently wide rivers, > 210 meters in width, the LST data set provides accurate water surface temperature measurements (mean error $\pm 0.46^{\circ}\text{C}$). By comparing surface temperature measured by LST to the temperature measured in situ at depth in the meandering Koyukuk River and an adjacent oxbow lake, we corroborate expectations that remote sensing of river surface temperature is an accurate representation of the temperature throughout the river water column, although it is not for lakes due to their thermal stratification. We examine the spatial and seasonal patterns that emerge in our remotely sensed temperature maps and find that water temperature closely matches local air temperature, but with a lag due to higher thermal inertia. We also identify deviations in water temperature from air temperature due to other forces that influence water temperature, including mixing with intersecting water bodies, upstream watershed temperature, and mixing within individual bodies. These forces can create large ($\sim 5^{\circ}\text{C}$) variations in contemporaneous surface water temperature across a floodplain, a significant magnitude of variation for environmental processes that are modulated by temperature, but a variation that is challenging to capture with other methods besides remote sensing.

We conclude that satellite-based remote sensing of water temperature can and should be applied to studies of Arctic riverine environments. Potential important applications include using LST to help predict the rates and processes of thermophysical riverbank erosion, as we find that LST-derived river surface temperature is demonstrative of the temperature of water in contact with permafrost-bearing riverbanks. Additionally, we demonstrate LST-derived river temperatures can be used to identify locations such as confluences that could act as lifesaving thermal refuges for migrating fish, especially crucial for declining salmon populations that are critical for Arctic communities (Jacob et al., 2010; Westley, 2020; Thorstad et al., 2021; Biela et al., 2022). Particularly in remote, data-poor environments, these remote sensing data sets can be key to understanding the thermal landscapes of riverine corridors and to examining their complex processes and implications.

In this study, we take advantage of the contiguous spatial coverage provided by remote sensing temperature data, but future work should also take advantage of its long temporal record. Many studies of river temperature's response to climate change have relied on in situ temperature gauges (e.g. Kaushal et al., 2010; Isaak et al., 2012), but the gauges present in Alaska were placed too recently (largely within the past 15 years) to record a climate change signal. Prior studies of climate change effects on Arctic rivers such as on salmon populations typically rely on air temperature as a proxy for water temperature (e.g. Biela et al., 2022), but it is unclear that both are responding the same to climate change. However, the LST data record goes back to 1982, long enough to record a climate change signal. Future work should use these remote sensing data to directly determine the effects of climate change on Arctic river temperature. By combining the long temporal record with the continuous spatial coverage, future work could also identify any effects of climate change on rivers' along-river thermal profiles. Finally, these datasets have global coverage and can be applied anywhere. The coverage, accuracy, and long temporal record of LST allow us to understand the effects of climate change on the temperature of sufficiently large rivers all over the world.

Future work to use remotely sensed thermal data to examine either the spatial or the temporal patterns of river temperature would benefit from higher spatial resolution and greater accuracy. While we have demonstrated the great potential of the Landsat LST dataset, we were limited to water bodies >210 m in width due to the low inherent spatial resolution of 100 m/pixel and the applied upsampling and interpolation to 30 m/pixel. If future Earth-orbiting missions were able to gather thermal data at higher resolution such as the 60 m/pixel of Landsat 7 or possibly even higher, this would greatly increase the number and diversity of water bodies whose temperature could be examined with this type of data. Additionally, for identifying subtle climate trends in water temperature and for understanding the thermal forces acting on watersheds in detail, temperature data with greater accuracy and smaller variation from measured in situ data would be beneficial. The greatest source of uncertainty is the atmospheric correction process, particularly due to atmospheric moisture (Hulley et al., 2012). Atmospheric correction pipelines are consistently evolving, so new, more rigorous algorithms may be able to improve data quality for applications across the globe.

5.3 Conclusions

The surfaces of planets tell the story of their natural history. From the minerals to the geomorphic features to the biosphere, these features record the planets' past. On Earth and throughout the solar system, water is one of the most important forces that has shaped and continues to shape planetary surfaces. From the active liquid water of our water-rich blue planet of Earth to the traces of ancient water long since disappeared on our red neighbor Mars, if we can understand the effects that water has had on shaping planetary surfaces, we can gain a great deal of insight into the history of these bodies. Remote sensing provides one of the most powerful tools we have to examine these processes and put together the story of their aqueous processes. Where it is difficult to conduct in situ field work (like the remote Arctic) or nigh impossible (like Mars), satellites provide us with eyes in the sky to examine aqueous processes on a detailed regional scale but also the ability to put those regions in a global context. Though this

work has focused on water, it has led us to conclusions about volcanism, interior processes, environmental redox state, salmon ecology, greenhouse gas release, and more. Beyond our conclusions about Al-phyllsilicate formation on Mars or river temperature in Alaska, our results demonstrate the role that water plays as the lynchpin of connecting and understanding geologic and environmental processes throughout the Solar System.

5.4 References

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