Aluminum phyllosilicate and jarosite–alunite formation from probable volcanic ash deposits across Mars

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Introduction: Clay minerals in Mars' Noachian terrains record ancient water-rock interaction and potentially climate [e.g. 1, 2]. Fe/Mg-phyllosilicates, e.g., smectite (Fe endmember nontronite to Mg endmember saponite), have been detected across Mars. Al-phyllosilicates, including kaolinite and montmorillonite, have also been detected in small 1s–10s km^2 exposures of Noachian bedrock in a few select regions: Nili Fossae, Mawrth Vallis, Valles Marineris, Libya Montes, Terra Sirenum, and north of Hellas Planitia (Fig. 1) [e.g. 2]. These Al-phyllosilicates can indicate a higher degree of alteration of a basaltic protolith than Fe/Mg-phyllosilicate, as was previously suggested [2–5]. Detections of sulfate minerals in the jarosite–alunite solid solution and reexamination of meters-scale stratigraphic relationships in Mawrth Vallis and Terra Sirenum have indicated acidic weathering as potentially contributing to Al-phyllosilicate formation [6–10, 5].

The Al-phyllosilicate in the Nili Fossae region has been previously interpreted to be part of a pedogenic leaching sequence from a basaltic protolith [3]. However, that analysis was before the detection of some jarosite deposits in the region [6] and without the most recent CRISM and HiRISE images. We therefore reexamined the Al-phyllosilicate in the context of its relationship to jarosite and with all available imagery. Here we present results from that analysis and compare them to the alteration mineralogy at Mawrth Vallis and Terra Sirenum. We examine what these sequences demonstrate about Mars' evolving geology and alteration processes.

Methods: To characterize and evaluate the Al-phyllosilicate assemblages in Nili Fossae, we examined the 167 available map-projected targeted reduced data record (MTRDR) corrected and de-noised images of this region acquired in visible/shortwave-infrared by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) [11]. Al-phyllosilicates, Fe/Mg-phyllosilicates, jarosite, alunite, and hydrated silica were identified and mapped using Gaussian fitting as described by [12, 13]. We examined the mineral textures, spatial relationships, and stratigraphy using a combination of High-Resolution Imaging Science Experiment (HiRISE) imagery, High Resolution Stereo Camera (HRSC) digital elevation models, and CRISM mineral maps as described by [12, 13]. We then compared these results to prior work that examines the formation of Al-phyllosilicate in Mawrth Vallis and Terra Sirenum

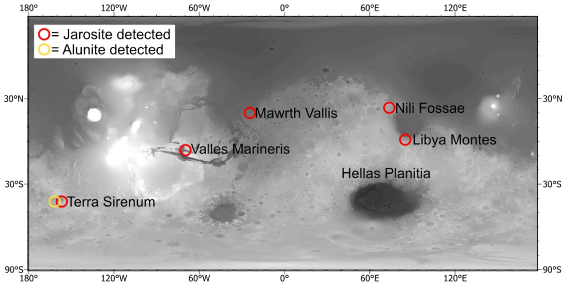

Figure 1: Global map of the six regions that contain Al-phyllosilicate-bearing units that appear to stratigraphically overlie Fe/Mg-phyllosilicate-bearing units. Colored circles indicate regions where nearby jarosite and/or alunite has been detected alongside Al-phyllosilicate.

Results:

Nili Fossae: We identified 56 images that contain Al-phyllosilicate, most with multiple deposits or exposures. Based on the Gaussian fitting parameters and visual examination of the spectra, we determined that all the Al-phyllosilicate in Nili Fossae is kaolinite-bearing, without other Al-phyllosilicate identifications. We found that the kaolinite is always associated with adjacent Fe/Mg-phyllosilicate. As expected [3], kaolinite-rich terrain with accompanying Fe/Mg-phyllosilicate primarily occurs close to the fossae and the edge of the Isidis impact basin, while opal primarily occurs on plains to the southwest and is found alongside Fe/Mg-phyllosilicate, illite and chlorite. We searched for but did not identify montmorillonite, alunite, or iron oxides associated with the kaolinite deposits [13].

In agreement with prior findings [2, 3], the kaolinite in Nili Fossae consistently occurs stratigraphically above Fe/Mg-phyllosilicate. These two minerals are almost never mixed at the scale of a CRISM pixel (18 m). In almost all cases, the boundaries between the kaolinite and the Fe/Mg-phyllosilicate are sharp and represent unconformities. These minerals correspond to discrete textural units (Fig. 2). 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 structure suggests they are formed of sedimentary deposits. Where there are clearer exposures, the kaolinite units demonstrate lamination, with layers that contact the Fe/Mg-phyllosilicate unconformably. The Fe/Mg-phyllosilicate units mostly appear knobby, rough, and unlaminated, though some patches have similar fractures to the kaolinite. The different textures of the kaolinite and the Fe/Mg-phyllosilicate and the unconformities between them indicate that they did not form as part of a leaching sequence but instead formed from two different protoliths.

The texture of the deposits, including exposed layers and association with flat layered plateaus, suggests that the kaolinite formed from transported sedimentary material. This scenario is supported by the apparent association of kaolinite with large (10s of km)-scale topographic lows including impact craters and large eroded depressions (Fig. 3). Many of these topographic lows show clear evidence for drainage pathways and sediment accumulation. The kaolinite sediment or its precursor likely accumulated in these topographic lows due to aeolian and/or surface water sedimentary transport processes [13].

An airfall deposit of ash or pyroclastics produced by local volcanism is the most straightforward process to produce the observed texture and stratigraphic context of the kaolinite unit regionally. The ash would have been deposited across the region, some of which sintered and remained on intercrater plains and plateaus to weather in-situ into kaolinite, but much of which accumulated in basins where large kaolinite deposits formed. The mineralogy of the kaolinite units is consistent with formation from an Al- and Si-rich (non-mafic) ash of a possible felsic to intermediate composition [13].

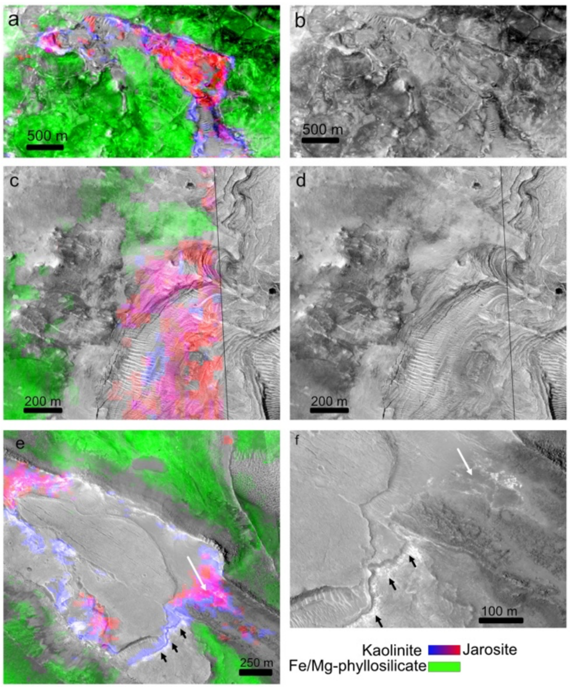

Figure 2: Mineral maps and high-resolution imagery demonstrating the textures of kaolinite, jarosite, and Fe/Mg-phyllosilicate in Nili Fossae. a–d) Well-mixed layers of kaolinite and jarosite unconformably contacting knobby, unlaminated Fe/Mg-phyllosilicate in CRISM image HRL0000AB0A e–f) Irregularly-fractured kaolinite exposed around the edges of a plateau with patches of jarosite in CRISM image FRT0000A053. The black arrows indicate kaolinite eroded out of the cliff face, and the white arrow points to a discrete patch of jarosite in contact with kaolinite.

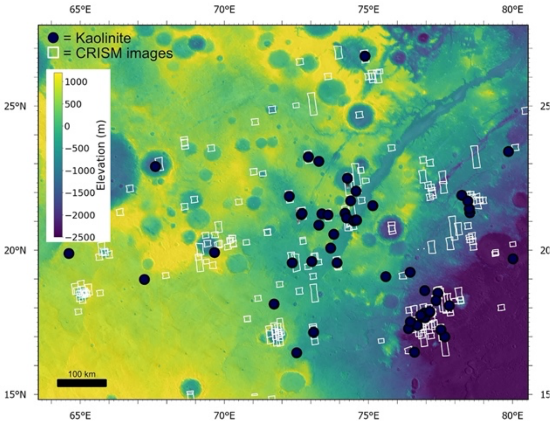

Figure 3: Topographic context of all kaolinite deposits in Nili Fossae. Basemap is the MOLA 463 m DEM (USGS).

Of the 56 kaolinite deposits in Nili Fossae, five were found to be closely associate with jarosite, mostly in topographic lows. This jarosite occurs in two contexts: (1) kaolinite and jarosite are well-mixed, or (2) jarosite forms small discrete patches corresponding to darker material in HiRISE imagery, which suggests authigenic precipitation of jarosite within the kaolinite (Fig. 2). These assemblages indicate that jarosite and kaolinite either formed contemporaneously, or jarosite post-dates kaolinite.

To form jarosite, there must be sufficient Fe and S present in a system during acidic alteration. In Nili Fossae, jarosite precipitates alongside kaolinite, an Al-phyllosilicate, with no other Fe minerals present. In environments that are more enriched in Al relative to Fe, alunite forms instead of jarosite during acidic alteration [14]. The presence of jarosite alongside kaolinite in Nili Fossae therefore suggests that Fe is supplied to the system by the altering fluid. We propose that groundwater could become Fe-enriched by dissolving Fe as it percolates through the >100 m of Fe/Mg-phyllosilicate underlying the kaolinite. We also propose that jarosite may not form alongside the Fe/Mg-phyllosilicate in this region because the requisite S to form jarosite is provided by the kaolinite protolith [13]. This scenario may be consistent with the protolith's proposed origin of a volcanic ash, as ashes are rich in S from adsorbed sulfuric gases released by volcanism [15].

Mawrth Vallis: The Mawrth Vallis Al-phyllosilicate deposits are composed of a lower unit of montmorillonite and an upper unit of kaolinite, both likely mixed with a hydrated silica component [16]. This Al-phyllosilicate-bearing unit is unconformably draped over the underlying Fe/Mg-phyllosilicate [16, 17]. Data from HiRISE, the Mars Orbiter Camera, and THEMIS show that the phyllosilicates are layered on the scale of meters [17, 18]. This stratigraphy is consistent with an airfall deposit of a fine-grained pyroclastic deposit like a tephra or ash [4, 17]. A pyroclastic origin for the Al-phyllosilicate in this region is also supported by the detection of the hydrated silica minerals allophane and imogolite above the kaolinite-bearing unit [10]. These minerals form terrestrially during the early stages of weathering of volcanic ashes at pH of around 5–7 [19].

A small number of jarosite deposits have been detected across Mawrth Vallis. Some of the largest deposits appear to overlie the Al-phyllosilicate-bearing unit and differ from it in texture. It has been proposed that acidic fluids enriched in S from dissolution of volcanic gases or ash may have produced this jarosite in small surface ponds from alteration of a pyrite-bearing layer deposited on top of the Al-phyllosilicate [4, 7, 20], though the source of the pyrite-bearing layer is unclear.

We observe additional jarosite deposits in the region that are spectrally mixed with and texturally similar to adjacent Al-phyllosilicate. These assemblages suggest formation of jarosite from the Al-phyllosilicate protolith like we propose for Nili Fossae. In this case, it is possible that acidic fluid in Mawrth Vallis was produced by S sourced from the Al-phyllosilicate and jarosite protolith, and the requisite Fe was leached from the abundant surrounding Fe/Mg-phyllosilicate. Because the texture and context of these jarosite deposits differ from those characterized by [4, 7, 20], jarosite may have formed via two different processes or protoliths in this region.

Terra Sirenum: The Terra Sirenum region contains two types of Al-phyllosilicate deposits: thin Al-phyllosilicate units within Eridania Basin and thick (60–150+ m) Al-phyllosilicate layered deposits outside of the basin [e.g., 5]. Eridania is a purported ancient sea on the edge of Terra Sirenum [21] that contains possible marine hydrothermal deposits. Jarosite is associated with Fe/Mg-phyllosilicates in these deposits, likely formed from later alteration of Fe-sulfides under oxidizing conditions [22]. 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 [23]. This has been interpreted as a pedogenic leaching sequence, as there is a diffuse contact with no clear textural distinction between these phyllosilicates [5, 24]. The presence of associated jarosite and alunite largely in veins and spectral evidence of acid-altered Al-phyllosilicate indicates alteration by acidic fluids in possible groundwater flow [5, 25].

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 scenario is indicated by fine layers in the Al-phyllosilicate and diminishing thickness of the unit away from the volcano Arsia Mons [5]. These Al-phyllosilicates, largely kaolinite with some possible montmorillonite, are found across the region but are concentrated in Columbus and Cross craters. In these regions, Al-phyllosilicate is associated with alunite. In Columbus Crater, the kaolinite may have formed from direct precipitation out of a deep paleolake, with alunite precipitating later from remnant shallow ponds [26]. In Cross Crater, substantial alunite in association with kaolinite suggests more extensive alteration by acidic fluids [9, 27]. The alunite largely occurs in veins, perhaps due to the upwelling of acidic groundwater. This groundwater may have become acidic though sulfur-enrichment from underground magma sources [5, 9]. Little Fe/Mg-phyllosilicate is exposed outside of Eridania, though small amounts in crater ejecta indicate the presence of some at depth beneath the Al-phyllosilicate unit [5].

Discussion:

Comparison of regional protoliths and weathering processes: In Nili Fossae, Mawrth Vallis, and Terra Sirenum, it appears that at least some of the observed Al-phyllosilicates 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. In Nili Fossae and Mawrth Vallis, the acidic sulfate that is formed alongside Al-phyllosilicate is jarosite as opposed to alunite in Terra Sirenum. At least some of the jarosite in Nili Fossae and Mawrth Vallis is mixed with Al-phyllosilicate, indicating formation of both minerals from the same protolith. In these regions, we propose that groundwater leached Fe out of the surrounding 100s of m thick Fe/Mg-phyllosilicate. This could explain the difference between Nili Fossae and Mawrth Vallis versus Terra Sirenum. There is at least some Fe/Mg-phyllosilicate underlying the Al-phyllosilicate in Terra Sirenum, but its extent is unclear [5], and there may have been insufficient Fe in the fluid to produce jarosite and suppress alunite.

Additionally, the Al-phyllosilicate in Nili Fossae appears to be exclusively 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^{2+} perhaps due to high porosity of its volcanic ash, and/or the Al- and Si-rich protolith in this region had a lower concentration of these ions originally [28].

Implications for Mars aqueous alteration:

Previous interpretations of Nili Fossae, Mawrth Vallis, and Terra Sirenum, in addition to other Al-phyllosilicate bearing regions on Mars, have proposed that the Al-phyllosilicate formed as part of a leaching sequences of basalt [e.g., 2–4]. This requires an extensive amount of aqueous alteration [29, 30]. If the Al-phyllosilicate protolith is instead an Al/Si-rich volcanic ash, less cumulative contact with water is likely required to produce the observed Al-phyllosilicate. This is due to the initially higher concentration of Al in the protolith and because ashes are glassy and porous and therefore weather rapidly.

We can constrain the duration of aqueous activity required to produce the Al-phyllosilicates in these regions. While not an exact match for the proposed chemistry of the ash protolith, terrestrial weathering rates for the conversion of glassy ultramafic rock to dioctahedral phyllosilicate range from 0.01–0.001 mm/year [31]. Using these rates and the models developed by [32] and assuming a process of low-temperature top-down weathering from meteoritic water, 2.5–14 million cumulative years of weathering would be required to produce ~100 m of kaolinite, the thickest deposits in Nili Fossae or Terra Sirenum, or around half that time to produce the ~40 m of kaolinite in Mawrth Vallis [5, 13, 17]. With further bounds on the temperature and pH of formation that could be identified with Mars sample return and experiments on the alteration of ashes under Mars-like conditions, this weathering duration could be identified with significantly less uncertainty and therefore aid greatly in the understanding of Mars' early climate and hydrosphere.

Implications for Mars volcanism:

If Al-phyllosilicate in Nili Fossae, Mawrth Vallis, and Terra Sirenum all formed through alteration of Al/Si-rich volcanic ash as has been proposed [5, 10, 13], this has potentially significant implications for our understanding of Mars volcanism. Mars has had extensive volcanism, but it is thought to largely be effusive rather than explosive. Effusive volcanism produces little ash or other pyroclastic deposits. This prevalence of effusive as opposed to explosive volcanism has been an open question in Mars geology because explosive volcanism is expected to be more common on Mars. Due to Mars's low surface atmospheric pressure which causes rapid expansion of even small amounts of dissolved gases [33] and the abundance of volatiles in Mars's crust [e.g. 34], it has been proposed that explosive volcanism should be widespread [35]. However, this is not reflected in the geologic mapping, in which evidence of effusive volcanism such as large shield volcanoes and low-viscosity lava flows is much more common [36, 37].

While effusive volcanism dominates Mars's geologic record, there is some evidence for explosive volcanism and related pyroclastic deposits. This evidence includes paterae with apparent caldera and evidence of extensive physical erosion, suggesting they are composed of a friable material like pyroclastic deposits [38– 41]. There is also purported evidence of explosive volcanism at volcanoes near areas of exposed Al-phyllosilicate. This includes Arsia Mons, the proposed source of volcanic ash at Terra Sirenum [5], paterae in Arabia Terra that may have deposited ash in Mawrth Vallis [4], and Syrtis Major, which could be a possible source of ash in Nili Fossae.

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 [42]. However, the analysis of Al-phyllosilicate and the interpretation that a large number of the deposits are best explained by an ash protolith provides new evidence for the extent of explosive volcanism in Mars's past. This analysis also suggests that these ash deposits were more Al/Si-rich than basaltic or otherwise mafic compositions, which could help constrain compositions of ancient Mars lavas. Future analysis is needed to better understand how these Al/Si-rich ashes could form and what the implications are for Mars's internal processes and evolving volatile budget.

Future work: We are applying the Gaussian fitting method that we used for automatic mineral detection in Nili Fossae to identify Al-phyllosilicate and its accompanying minerals in CRISM imagery across the other Al-phyllosilicate bearing terrains: Mawrth Vallis, Terra Sirenum, Valles Marineris, Libya Montes, and north of Hellas Planitia. We will combine the resulting mineral maps with high-resolution imagery and DEMs as we did for Nili Fossae to characterize the textures and stratigraphic contexts of the mineralogic units. With these data, we seek to better understand how Al-phyllosilicate and jarosite–alunite formed across Mars and their implications for the evolution of Mars's climate and geology.

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