PLATEAU WETLANDS AT MAWRTH VALLIS AND POSSIBLE IMPLICATIONS FOR CLAY AND OXIDE LAYERS IN GALE CRATER.

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Introduction: Noachian outcrops in the Arabia Terra region expose a thick (~150m) stack of light-toned deposits that have near-IR spectra consistent with a variety of clay minerals [1-10], and these are best exposed around Mawrth Vallis. While origins proposed for these clays include lacustrine, diagenetic, hydrothermal, and pedogenic, few have been able to explain the full diversity of clay minerals, and good terrestrial analogs have been lacking. In this study, we provide an overview of the clay/sulfate mineralogy of Mawrth Vallis and propose a geologic framework for interpretation based on terrestrial paleosol sequences.

Paleosol sequences: The majority of terrestrial non-marine clays are formed in soils. Buried soils are preserved as paleosols, and can be used to reconstruct ancient surface environments and climates [11,12]. When sediments are repeatedly deposited (*e.g.*, alluvial, deltaic, or volcaniclastic sediments), paleosol sequences form that can track rapid paleo-environmental changes. Paleosols can be regionally extensive, especially volcaniclastic paleosol sequences like in the Painted Desert [13,14] and Painted Hills [15]. Volcanism has been proposed as the origin for the extensive sediments at Mawrth Vallis, and the observed clays are all common pedogenic minerals.

Mawrth mineralogy: The lower ~100m of the Mawrth Vallis sequence exhibits 2.29 μm bands characteristic of Fe/Mg-smectites (*e.g.*, nontronite). In contrast, the upper ~50m exhibits bands near 2.20 μm, consistent with Al-rich phases, but with minima varying from 2.16-2.21 μm. This suggests significant variation in mineralogy, from alunite (2.16 μm) to beidellite/allophane (2.18-2.20) to kaolinite (2.20) to Al-smectites (2.21) [9,10]. Phases other than Al-smectites are correlated with red spectral slopes between 0.7-1.8 μm (Fig. 1c), which are consistent with ferrous clays (chlorites/smectites/micas or pedogenic "green rust") [10]. Localized 2.31 μm bands within the red slope regions are consistent with saponite or Fe(II) smectites [16]. Red slopes are also observed near the boundary between the upper and lower units, but not in all exposures. Some exposures of this boundary also exhibit 2.27 μm bands, consistent with acid-treated smectite, or, perhaps, jarosite [7,17]. On some large slopes, this material extends down into the lower unit.

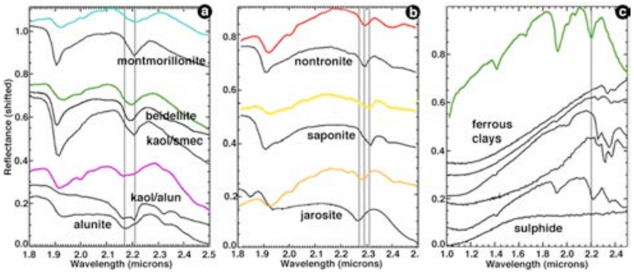

Figure 1: *Example CRISM FRT3BFB ratio spectra (colors) and selected lab spectra of (a) Al-clays/sulfates, (b) Fe/Mg-clays/sulfates and (c) Fe(II)-clays/sulfide.*

Smectites, climate, and parent material: Smectites are common soil minerals, and smectite-dominated (~70-95 wt.%) soils typically form in semi-arid climates [14]. Smectites generally indicate rain, as opposed to snow/ice-melt, as seasonal melting causes a pulse of rapid weathering that favors poorly-crystalline phases like allophane/halloysite [18]. If the Mawrth smectites are pedogenic, they imply a long-lived semi-arid climate with precipitation in the form of rain.

Smectite compositions are strongly influenced by their parent material. On Earth, nontronite only forms in mafic soils, Mg-smectites only form from Mg-rich parents (e.g. serpentinite), while common silicic soils form Al-smectites like montmorillonite [19, 20]. Thus, the change in smectite composition from Fe/Mg- to Al-smectites at Mawrth strongly suggests that the parent material also changed, from mafic to more silicic.

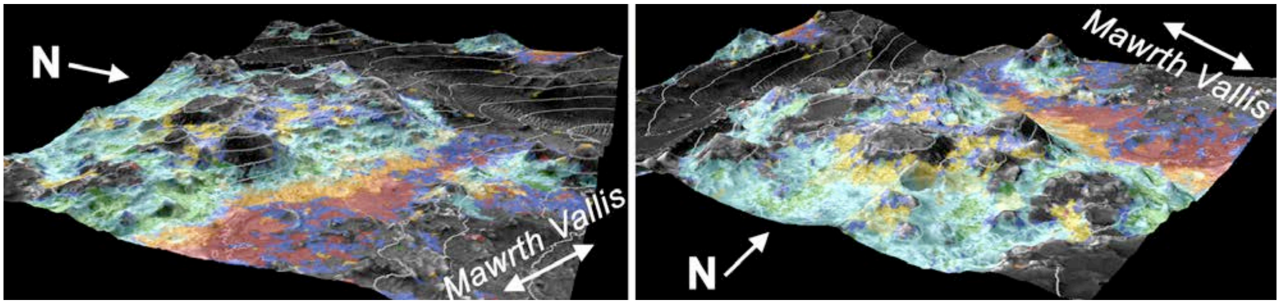

Figure 2: *Two views of a map of spectral units in CRISM FRT3BFB, draped over HiRISE DTM. Yellow: 2.31 μm band, Green: 2.16-2.20, Blue: 2.21, Orange: 2.27, Red: 2.29, Purple: other hydrated minerals. View is 6 km wide.*

Reduced iron and local waterlogging: When soils become persistently saturated by standing water, they are cut off from atmospheric oxidants, and become reducing. Reduced iron (Fe(II)) in the form of ferrous clays or poorly crystalline "green rust" is a key signature of waterlogged soils, and is produced from ferric iron liberated by carbonic acid-driven hydrolysis [14]. We propose that the patchy Fe(II) spectral signatures at Mawrth [10] are consistent with local waterlogging in a wetlands-type surface environment. As these deposits are on the plateau above Mawrth Vallis and Chryse Planitia, the waterlogging was not due to location in a topographic low, but instead must have been due to a perched water table caused by an impermeable subsurface layer. The apparent concentration of Fe(II) near the boundary with the Fe/Mg-smectite unit suggests that this unit was the cause of poor drainage, and was thus clay-rich enough to be impermeable.

Acid-sulfate soils and groundwater flow: The co-ocurrence of possible alunite/allophane/kaolinite with Fe(II) at Mawrth Vallis suggests that the waterlogged areas had a different aqueous chemistry than the surrounding neutral and well-drained Al-smectite soils. While kaolinite/beidellite/allophane in soils are typically indicative of greater leaching in humid climates [21], their patchy distribution and association with Fe(II), indicating poor drainage, rules out a climatic influence. However, all of these phases, as well as alunite, can also be produced through acid leaching of Al-smectites [22,23], suggesting that at least some of the waterlogged areas were moderately to mildly acidic.

On Earth, acid is produced in waterlogged environments through sulfide oxidation (*e.g.*, by water level drop and exposure to oxidizing atmosphere or possibly UV light) [23]. Sulfides can be from the parent material (*e.g.*, massive sulfide deposits) or from reduction of aqueous sulfate (*e.g.*, marine sulfate in coastal wetlands). The reduced Fe/S-bearing fluids can also oxidize upon emergence at lower elevations, forming additional acid-sulfate deposits [24]. At Mawrth Vallis, we hypothesize that Fe/S redox reactions due to fluctuating water tables in the upland terrains formed the Fe(II)/alunite/kaolinite/etc. assemblage, while drainage into lower-lying nontronite-bearing regions formed the jarosite/acid-treated smectite phase. New detections of possible Fe(II)-sulfate support this hypothesis [25].

Summary: The clay and sulfate mineralogy observed at Mawrth Vallis is consistent with pedogenic alteration in a sequence of surface environments. Based on this framework, we hypothesize that the Fe/Mg-smecite unit developed through repeated deposition and alteration of mafic volcaniclastics under well-drained and semi-arid conditions. Later, a series of more silicic volcaniclastics was emplaced under a similar semi-arid climate, and formed Al-smectites. However, drainage out of this unit was impeded by the underlying clays, so a perched aquifer was formed that caused local ponding at the surface. When the water table fluctuated, sulfide exposure and oxidation created acidic fluids that altered the Al-smectites to other silicic phases, and where these acidic fluids emerged at lower elevations, oxidation and alteration of the Fe/Mg-smectites produced mantles of jarosite.

Implications for MSL and Gale Crater: Two key mineral units at Mt. Sharp that will be investigated *in situ* by MSL are a layered, tens of meters-thick Fe/Mg-smectite-bearing unit just above a layered, ~10m thick, 200m wide hematite-bearing ridge that appears to be mantled onto Mt. Sharp [26, 27]. A proposed origin for the hematite ridge is emergence and oxidation of Fe(II)-bearing fluids from within the mound. However, the origin of the fluids is uncertain.

Our analysis of similar redox processes at Mawrth Vallis suggests that one possible origin of the fluids is from a perched aquifer within the mound, caused by infiltration of rain or snow melt and the presence of impermeable layers. Like the jarosite at Mawrth Vallis, the oxide ridge could be directly related to pedogenesis on the mound, which would have formed clays while liberating Fe(II). Thus, in this scenario the clay layers could be pedogenic in origin. The difference between the mineralogy at Gale and Mawrth Vallis is the lack of acid-sulfates at Gale, suggesting that Mawrth Vallis may have had much higher sulfur concentrations.

This hypothesis is testable *in situ* with MSL. If the clay layers are paleosols, they should exhibit cm-scale geochemical gradients and horizonation resolvable by ChemCam and APXS, as well as pedogenic textures at a variety of scales resolvable by MAHLI and Mastcam.

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