

MINERAL ASSEMBLAGES OF AL-PHYLLOSILICATE DEPOSITS ON MARS: IMPLICATIONS FOR LEACHING PROCESSES, WATER CHEMISTRY, AND ATMOSPHERE-WATER INTERACTIONS.

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Introduction: Layers enriched in Al-phyllsilicates (kaolinite or montmorillonite) overlying Fe/Mg-smectite-bearing units may be evidence for extensive leaching early on Mars [1-8]. This leaching hypothesis has implications for the hydrologic cycle on Mars and is consistent with a vertically integrated hydrologic system on early Mars [9-10]. Other hypotheses for the formation of Al-phyllsilicates include alteration of volcanic ash [3-5, 7], impact-driven hydrothermal systems [1, 11], formation of Al phyllsilicates elsewhere and deposition in these layers [2, 5, 12], interaction of layered phyllsilicates with acidic solutions [13], and weathering within or below ice deposits [14-16].

The Deccan basalts are a good spectroscopic analog to basaltic terrains on Mars [17]. We have studied samples from a weathered/altered section of Deccan basalts that has been extensively leached in a warm and wet climate [18-19] to assess the spectroscopic signatures of leaching with laboratory measurements and the mineral assemblages. Then, based on these analog results, we are surveying reported Al-phyllsilicate deposits on Mars with data from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) to construct their mineral assemblages and test the leaching hypothesis in order to better understand the environments on early Mars.

Analog Results: Relative degrees of alteration between the layers of weakly altered basalt, strongly altered saprolite, and laterite are readily seen in visible and near infrared (VNIR) spectroscopy (Fig. 1). The spectra of the saprolite samples contain no mafic signatures and are dominated by smectite clays, though XRD and Mössbauer analyses show retention of some primary mafic minerals. The laterite cap formed in an intense leaching and oxidizing environment [18-19] and is spectrally-distinct from the basalt and saprolite samples. Crystal field transitions from Fe^{3+} in hematite and goethite [20] and doublets near 1.4 and 2.2 μm from OH and Al-OH combination tones and overtones of kaolinite [21] characterize a distinct kaolinite and hematite assemblage. Chemistry data show leaching of mobile cations as the basalt is progressively weathered to a smectite-bearing saprolite and then a kaolinite- and hematite-bearing laterite. This kaolinite and Fe-oxide assemblage is consistent with other reported laterites on Earth formed from basalt [e.g. 22-23]. Additionally, a lateritic weathering profile developed on an ultramafic protolith and studied as a Mars analog has this same assemblage [24]. Thus analog environments of

extensively leached mafic rocks show a consistent assemblage of kaolinite-ferric oxide (hematite) lithologies over smectite saprolite.

CRISM Observations: Al-phyllsilicates have been identified at locations across Mars, but two regions, Nili Fossae and Mawrth Vallis, have extensive exposures of Al-phyllsilicates often in a clear stratigraphy overlying Fe/Mg-smectite-bearing units. In both regions, Fe-oxides are present but do not seem to be associated with specific rock types or assemblages. In Nili Fossae, there is a lack of Fe-oxides with kaolinite (Fig. 1). In Mawrth Vallis, Fe-oxides sometimes but not always occur with Al-phyllsilicates. These results are distinct from the remotely sensed signatures of leached analogs where both crystalline Fe-oxides and kaolinite can clearly be detected spectroscopically.

Discussion: The leaching model is a relatively simple model that can explain the formation of thin but extensive layers of kaolinite or montmorillonite stratigraphically above Fe/Mg-smectite layers. Furthermore, leaching commonly alters smectite to kaolinite on Earth and can produce stratigraphies with kaolinite overlying smectite [e.g. 25]. However, the resulting assemblages and Fe-oxide associations expected from weathering basalt under warm and wet conditions on Earth differ from the observations of Al-phyllsilicates on Mars. It is possible that the Al-phyllsilicates did form through leaching but under different Eh and pH conditions that mobilized and removed Fe. We must also evaluate models other than leaching.

Water chemistry and atmosphere interactions. Formation of kaolinite through leaching on Earth requires interaction with high volumes of fresh water with low silica and base cation activities, as lower water/rock ratios promote smectite formation or impede leaching of smectite to kaolinite [e.g. 26-27]. An easy way to deliver abundant dilute water to the surface is through rainfall, although melting of ice deposits (e.g. glaciers) would also produce freshwater. If the Al-phyllsilicates formed through leaching, the water may have been acidic. At very low pH, Fe^{3+} is mobile, so weathering of smectite by acidic fluids may have formed kaolinite but removed the Fe. The lack of Fe-oxides may also have implications for the redox state of the early Martian atmosphere. Fe^{2+} is more mobile than Fe^{3+} . If the early Martian atmosphere were reducing, Fe^{2+} in the original mafic minerals (e.g. olivine and pyroxene) might never be oxidized to form ferric oxides, and the Fe would be removed. The presence of

Fe-oxides in places but inconsistent association with any particular mineral in the stratigraphy in Nili Fossae and Mawrth Vallis, in contrast to the ubiquitous Fe-oxide association on Earth, could suggest that the Fe-oxides formed later on Mars.

Other models. We are evaluating more diverse models for the formation of Al-phyllsilicates on Mars to determine the expected mineral assemblages and see if any other model better fits the observations on Mars. Acidic weathering [13] could leach Fe, but more work should be done to constrain the pH at which kaolinite will precipitate but Fe will be mobilized. Alteration of volcanic ash or a more mafic protolith seems to form an assemblage containing Fe-oxide [24, 28-29]. The mineral assemblages cannot constrain the hypothesis suggesting that Al-phyllsilicates were deposited in sedimentary layers [2, 5, 12] because this hypothesis only explains the stratigraphy and not how the Al-phyllsilicates initially were formed. More work should look at the precipitation of Fe-oxides and kaolinite at high temperatures in hydrothermal systems. Leaching of smectite to form kaolinite from basal melting of glaciers [15] could isolate the waters from the atmosphere and leach smectite in a reducing environment, even if the atmosphere was oxidizing. It is unclear what the expected Fe-oxide associations would be if the Al-phyllsilicates formed in acidic brines within the ice sheet [14, 16].

If the early Mars atmosphere was oxidizing and Al-phyllsilicates formed at the surface or in the shallow subsurface, crystalline Fe-oxides would be expected to precipitate and be associated with kaolinite. However, if the atmosphere was reducing, Fe would be unlikely to oxidize and would have either been removed or remained as secondary ferrous minerals [30]. If the Al-

phyllsilicates formed deeper in the subsurface in groundwater or hydrothermal systems and the altering fluids had not recently been in contact with the atmosphere, conditions may have been similarly reducing, and Fe-oxides would not be expected. At lower pH, Fe may be mobilized and removed [30]. Future work will continue to evaluate the leaching model for Al-phyllsilicate formation and look at other models. We will also incorporate different fluid and atmospheric chemistries and alteration at different temperatures.

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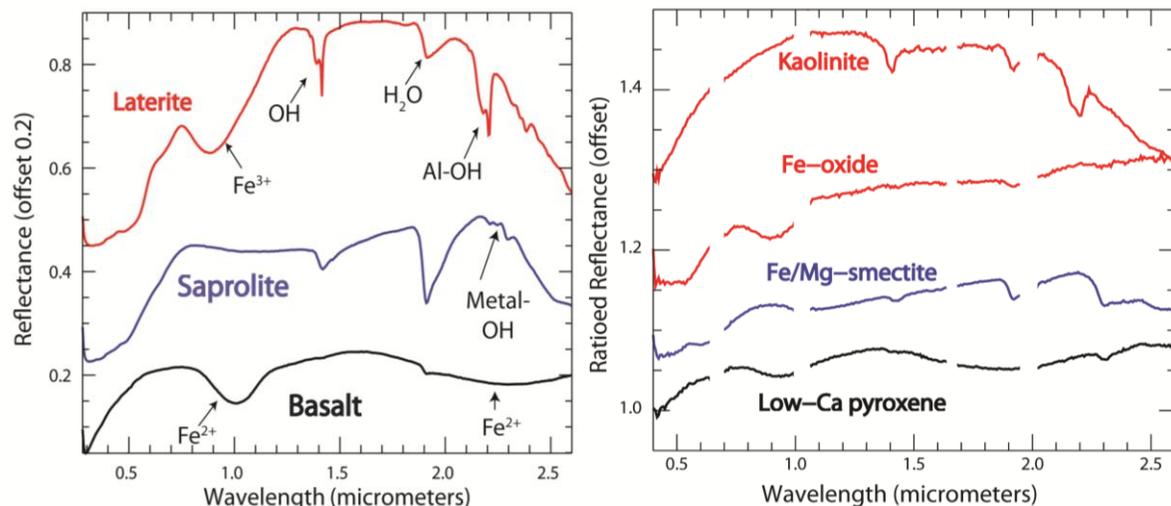


Fig. 1: VNIR spectra of main units in Deccan analog (left). Spectra of similar units in Nili Fossae for comparison (left).