MODELING THE FORMATION OF SULFATES IN THE NOACHIAN CRUST OF MARS.

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Introduction: Major types of secondary mineralogy on Mars detected from orbit have transitioned from being dominated by phyllosilicates in the Noachian, sulfates in the Hesperian, and ferric oxides in the Amazonian **(Fig 1)** [1]. Sulfates are commonly found in layered Hesperian geologic units, which typicallyform in a more acidic environment [2]. The current Amazonian era is cold and dry, resulting primarily only in ferric oxides. Because of these mineralogical tendencies, identifying hydrated sulfates in the central peaks and ejecta of three craters in the Noachian-aged Tyrrhena Terra region of Mars was a cause for further study. In this abstract, we present our approach and preliminary results toward understanding the occurrence of these minerals.

Three-pronged Approach: Our investigation of the Noachian sulfates takes a three-pronged approach, building on our analysis of orbital observations [3]. From this initial investigation, we found that either epithermal or sulfide oxidation mechanisms, followed by a post-formation aqueous alteration, may have been responsible for the formation of the detected sulfates. Our next step is to determine if these processes could explain the coexistence of sulfates (polyhydrated sulfates and bassanite) with other minerals (chlorite, carbonate, and analcime). To do this, we utilize both geochemical modeling and laboratory experimentation approaches.

Our modeling approach consists of different numerical simulations of reactions that might occur in the geochemical environment using Geochemist Workbench. From these simulations, we expect toelucidate the reaction pathways that may have formed the secondary minerals co-existing with the sulfates. An isothermal partitioning coefficient experiment will also be conducted following geochemical modeling to, in particular, experimentally constrain pH as well as the fluid speciation necessary for sulfate/secondary mineral co-precipitation based on geochemical modeling constraints.

These experiments will allow us to visualize the geochemical behaviors of species during mineral formation under varying conditions. From this information, we hope to further constrain Mars' paleosalinity during the Noachian Era when chlorites, carbonates, analcime, and (presumably) sulfates initially formed. Furthermore, this data could provide insight on the cyclothem sequence in which the mentioned minerals formed.

Formation Process Hypotheses: We will explore four possible formation scenarios using geochemical modeling and laboratory experiments. Using Martian basalts as the primary rock composition is necessary for analyzing the reaction pathways for each of the secondary minerals. By exposing the starting basaltic composition to fluids with varying pH and measuring the minerals formed with scanning electron microscopy (SEM), confocal Raman imaging spectroscopy (CRIS) and energy dispersive x-ray (EDX) techniques as well as bulk powder X-ray diffraction (XRD) we can directly assess the applicability of the geochemical models. Furthermore, this approach will enable monitoring of the effects of environmental conditions, such as pressure, temperature, and redox conditions.

Acidic: For formation processes involving acidic conditions, we will look at epithermal and sulfide oxidation. We will examine epithermal and sulfide oxidation as possible formation mechanisms that could occur under acidic conditions. Epithermal processes are low temperature and pressure hydrothermal processes that produce sulfuric acid: aqueous dissolution of subsurface sulfur-bearing minerals (usually sulfide) bonds with primary cations (Fe^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}) [4] which then provides the necessary constituents to form sulfates, oxides, and sulfides. Additionally, sulfide oxidation can also produce sulfates through the reduction of Fe^{3+} [5]. Note that we do not anticipate the formation of chlorites, carbonates, or analcime directly from either of these processes, as these minerals favor more neutral to basic pH fluids.

Non-acidic (Neutral to alkaline): For non-acidic processes, we will study minerals precipitation from aqueous alteration of the starting Martian basaltic composition. Under these conditions, we expect to see the formation of chlorites (pH >7.5), carbonates (pH >8), analcime (pH >9), and sulfates (pH>7). However, these sulfates will most likely precipitate as Mg-sulfates since Fe-sulfates are highly soluble in non-acidic conditions [6].

Acidic + Non-acidic: This two-step process first involves acidic formation through either epithermal or sulfide oxidation followed by a secondary aqueous alteration process. Although we do expect to observe the initially-formed Fe-sulfate dissolve and reprecipitate as Mg-sulfate, there is a possibility that chlorite, carbonates, and analcime could also form during these secondary formation processes.

Non-acidic + Non-acidic: Another two-step process involves the introduction and reintroduction of aqueous fluids involved in alteration. The fluid pH levels, ranging from neutral to basic, will determine the resultant secondary minerals, since chlorite, carbonate, and analcime formation are very sensitive to pH. Regardless, we expect that Mg-sulfates to form in both processes.

Noachian Crustal Heterogeneity and Co-occurrence of Phyllosilicates: The investigation of Noachian sulfates could provide valuable information on the crustal heterogeneity of Mars. CRISM observations have confirmed the limited distribution of crustal sulfates across Tyrrhena Terra **(Fig. 1)** [3]. This finding suggests that the crustal composition of that region could potentially be heterogeneous with pockets of precursor materials throughout the subsurface. One possibility is that the precursor material only existed in a few spots within the subsurface of Tyrrhena Terra. Another possible explanation would be that groundwater demineralized the subsurface region, then reprecipitated minerals after displacement [2]. This work will be necessary for determining how the coexistence of Noachian crustal sulfates and other minerals identified could shape our understanding of the crustal heterogeneity of Mars.

Conclusion: Utilizing orbital observations, geochemical modeling, and laboratory experimentation, we hope to constrain the formation processes responsible for sulfates exhumed from Noachian-aged terrain, occurring alongside chlorite, carbonates, and analcime. Each of four hypotheses focuses on one or more formation processes related to epithermal, oxidizing, and aqueous alteration conditions, which are pH and temperature dependent. The results of this study could give us a better understanding of the Noachian crustal heterogeneity and its evolution.

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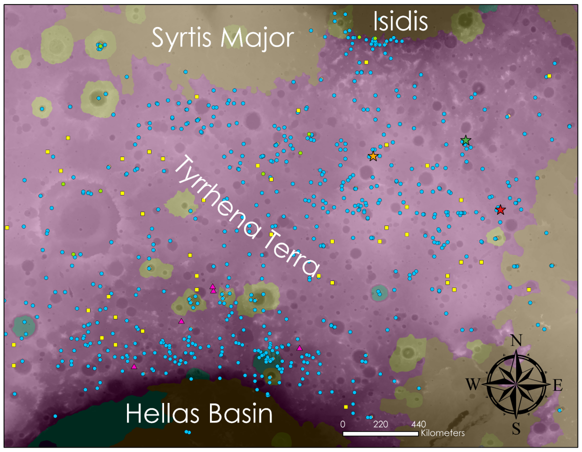

Figure 1. Regional context for the study area. The locations of the three craters in Tyrrhena Terra (labeled with yellow, green, and red stars) are shown relative to the distribution of hydrated minerals identified in CRISM targeted data [7], and the merged geologic units [8] overlain on greyscale MOLA topography. Phyllosilicates (Fe/Mg smectite, chlorite) are the dominant type of mineral within Noachian terrains with relatively few outcrops of chloride. Previously identified sulfate outcrops are near the southern region of Tyrrhena Terra, closer to the rim of Hellas Basin, and form in Hesperian-aged layered sedimentary deposits, distinct from the impact-exhumed sulfates.