

LOW-TEMPERATURE AQUEOUS ALTERATION ON MARS: INSIGHTS FROM THE LABORATORY.

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Introduction: The soil-like material mantling the Martian surface is geologically and chemically complex and holds information of past and present climatic conditions on Mars. Present knowledge of this surface material suggests that low-temperature, aqueous alteration may have been a major factor in forming the material that has been sampled thus far by the Viking and Pathfinder landers. The term aqueous alteration used here, encompasses a wide range of processes and includes both dynamic and stagnant water-rock and gas-rock alteration mechanisms. Much effort has gone into characterizing this material, and several models, based on a wide range of evidence, have given rise to many processes and resultant mineral/mineraloid phases that may be (or have been) of importance on the surface of Mars.

In terms of low-temperature aqueous alteration, the primary material being altered, that of the Martian basaltic crust, is somewhat constrained but the aqueous processes are not. The secondary alteration phases resulting from such processes have most likely been subject to sedimentary and physical mixing processes and as a consequence are well homogenized, somewhat obscuring their chemical signatures. Therefore, it is indeed a complicated and difficult problem to address the role that low-temperature aqueous alteration may have played in the formation of the Martian soil.

One way to approach such a problem is to do so experimentally. Experimental results from aqueous alteration experiments can highlight the most important chemical processes in a given system and the relevance of the laboratory system to a potential model can be assessed. Some workers have taken advantage of terrestrial systems, which have been used as templates for alteration on Mars. However, new constraints on Martian surficial processes can be made by testing these models experimentally by taking advantage of the present knowledge of the primary Martian basaltic crust.

A major conclusion of this work is how, among several other factors, aqueous alteration is highly dependent on primary starting material. In this paper, recent results of alteration experiments with synthetic basaltic material will be evaluated and their relevance to the Martian surface will be discussed.

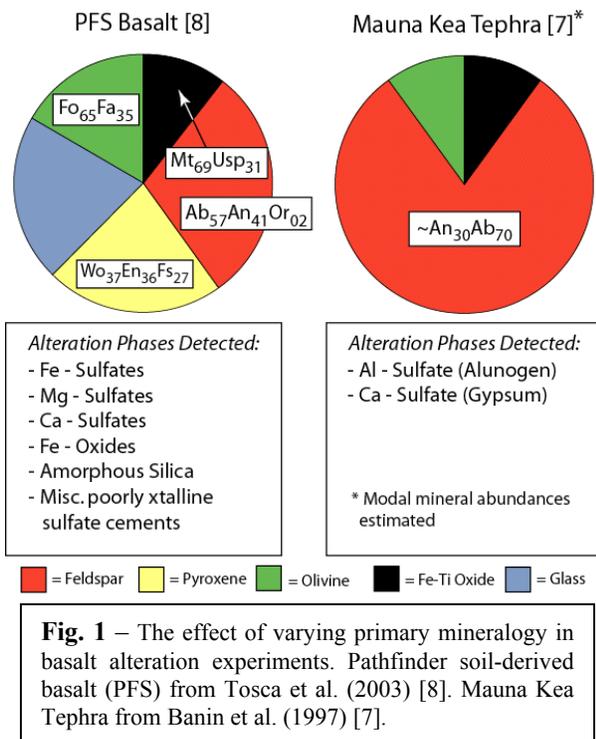
Low Temperature Aqueous Alteration on Mars: Several approaches to low temperature aqueous alteration on Mars have been taken to understand the origin

of the surface material as well as past climatic conditions on that planet.

The first of the major models for low temperature aqueous alteration on Mars includes palagonitization, which was first suggested by Gooding and Keil in 1978 [1]. The term palagonitization generally refers to the formation of palagonite, a hydrated, amorphous and isotropic alteration product of mafic glass [2]. The exact nature of palagonite, both chemically and mineralogically, is poorly defined and can contain a wide range of secondary, poorly crystalline minerals, most of which are combinations of smectites [2]. The initial gel-like palagonite is metastable, and over time may evolve into crystalline products such as clays, zeolites, oxides and carbonates [2]. The precipitation of palagonite and its associated poorly crystalline phases is dependent on many factors, which are important for other mechanisms of low temperature aqueous alteration as well and are discussed below. Palagonitization has been suggested to be important on Mars due to both the spectral similarities of palagonite material to the bright regions of Martian soils and the possibility that basaltic glass is somewhat abundant on the surface of Mars. In light of these observations, numerous studies have characterized terrestrial palagonites as analogs to Martian soil [e.g., 3-5].

Another major model for low temperature aqueous alteration on Mars is the acid fog model. This model involves the interaction of volcanically derived acidic volatiles with the Martian basaltic crust [6]. These volatiles may interact with primary rock in low fluid-rock ratios, causing mineral/glass dissolution. Subsequent evaporation of the fluid at a far-from-equilibrium state results in poorly crystalline alteration products which are composed mainly of sulfate and chloride salts. This model is proposed to have taken place in relatively recent Martian geological time (up to 1Ga) and its purpose is to explain the nature of the uppermost layer of surface material on Mars. This model was first experimentally tested in the laboratory by Banin et al. [7], who reacted Mauna Kea tephra with various acid mixtures and reported the precipitation of Ca and Al salts detectable by XRD. Tosca et al. [8] have further tested this model using synthesized basalt and glass with Pathfinder-derived bulk compositions and found that varying the starting material and aqueous conditions used in these experiments, significantly varies the secondary alteration minerals formed in this process. Figure 1 provides an example of the different alteration minerals Tosca et al. formed by

varying the primary mineralogy of the basalt. This approach and the putative alteration phases formed as a result, illustrates the importance of several different factors in low temperature aqueous alteration studies applied to Mars and will be discussed below in greater depth.



Brine interactions with the surface of Mars and their potential to form evaporites has been another suggested mechanism of alteration [9]. For example, the soluble salts found in nakhlites have been interpreted to result from evaporitic conditions on Mars [10]. One experimental study aimed at brine interaction on Mars was conducted by Moore and Bullock [11], where CO₂ charged water was interacted with SNC mineral mixtures for a period of one year. Modeling evaporation of the resulting fluid predicted Ca-sulfates, Al-hydroxide and carbonates.

Studies involving the importance of weathering on the surface of Mars also include a study by McSween and Keil [12], who evaluated chemical systematics of the Pathfinder and Viking soil data. The chemical trends produced by both palagonitization and the acid fog experiments performed by Banin et al. [7] were evaluated and it was determined that the chemical trend resulting from palagonitization may provide a suitable analogy to the Martian soils. However, McSween and Keil suggest that these changes are limited and that the soils contain components of different lithologies. Also, it has been suggested in this study and in others [e.g., 13] that complex sedimentary proc-

esses most likely have changed the compositions of the soils and that the homogeneous dust present on Mars may reflect the most abundant lithologies on the surface.

Other specific processes or secondary alteration phases, which may be important during low temperature alteration, have been suggested. For example, carbonate formation has been suggested to be important on Mars, despite little evidence for carbonates at the surface. The postulation of high partial pressures of atmospheric CO₂ at one time in the past have led to the suggestion of carbonate reservoirs acting as a sink for CO₂ [e.g., 14].

Sedimentary silica is another example of potentially important secondary alteration phases and has been suggested by McLennan [15], who notes that silica is highly mobile during basalt alteration and that secondary silica phases may have been formed and subsequently distributed in sediments. In light of this observation, McLennan suggests that this may explain some of the high silica features observed on Mars.

The origin of pre-terrestrial secondary alteration materials present in SNC meteorites has been studied experimentally by Baker et al. [16] and provides an example of basalt alteration in experimental settings. In this study, CO₂, S and Cl rich waters were passed over crushed Columbia River basalt at two different temperatures, 23 and 75°C. The low temperature experiments formed calcite, magnesite and opal-CT. Resulting fluid compositions were also modeled for equilibrium evaporite assemblages.

Laboratory Systems – Insights from Synthetic Basalt Alteration: The models discussed have several aqueous geochemical processes in common and it is important to determine what these processes are as well as the factors that govern them. Using synthetic basalts and basaltic glass of Martian composition as a starting point for aqueous alteration has begun to provide important information about fundamental aqueous processes involved with basalt alteration of such a chemically unique host rock. These processes and supporting observations from the laboratory are discussed in this section.

Similar to how a rock is defined as an aggregate of minerals, aqueous basalt alteration can be defined as an aggregate of mineral alteration processes. The contributions to an aqueous system from the alteration of individual mineral/glass phases can vary significantly. Therefore, the fluid chemistry and resultant secondary minerals formed will be a direct result of the primary phases being altered. Although there are countless factors involved in aqueous environments, the discussion here is limited to those that are common among the major models proposed for the Martian surface. These include dissolution and its effect on fluid chem-

istry, and precipitation processes forming secondary alteration phases.

Dissolution: Interaction of basalt with fluids in most systems results first in dissolution. Dissolution is a major process in low temperature alteration, because dissolution rates and mechanisms largely determine fluid chemistry. The dissolution rates and mechanisms of mafic minerals and glasses differ significantly from each other and are dependent on several processes, including temperature, fluid composition, fluid dynamics and the structure of the material being dissolved. Variation of these factors has the potential to change dissolution rates by orders of magnitude. Laboratory investigations using synthetic basalt have shown that in low temperature static-fluid systems, the stoichiometry of dissolution is mainly dependent on acid concentration [8]. In systems with low pH values, dissolution proceeds stoichiometrically, releasing the components of the mineral/glass in to solution in the same proportions as the solid. As pH rises and becomes less aggressive but still acidic, dissolution proceeds non-stoichiometrically, where some components are released preferentially to others. This is the case in most natural waters on Earth and as a consequence, is a key factor in determining fluid composition.

Non-stoichiometric dissolution is controlled significantly by the crystal chemistry of the phase being dissolved. Silicate minerals dissolving non-stoichiometrically readily release ionically bonded non-structural constituents. Dissolution of orthosilicates such as olivine liberates Fe^{2+} , Mg^{2+} and H_4SiO_4^0 rapidly, due to the breaking of either Mg-O bonds or Fe-O bonds, which can destroy the entire structure of the mineral [17]. Under oxic conditions where Fe^{2+} may be oxidized to Fe^{3+} , which is insoluble, dissolution may proceed non-stoichiometrically. In framework silicates such as feldspars, the K^+ , Na^+ and Ca^{2+} ions are released initially, while the aluminosilicate framework is hydrolyzed and destroyed at a much slower rate. The destruction of the residual framework is also dependent on the amount of Al present, as Al-O bonds are broken more easily than Si-O bonds [17]. In pyroxenes, cations occupying the M2 sites are preferentially released during this process. This can include Ca^{2+} , Fe^{2+} and Mg^{2+} , depending on the chemistry of the pyroxene. The residual structure of the pyroxene is then composed of M1 cations cross-linking chains of silicate tetrahedra. Destruction of the residual layer then proceeds by the breaking of M1-O bonds and Si-O bonds.

In basaltic glass, network-modifying cations such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} and Fe^{2+} are released preferentially to network-forming cations such as Si^{4+} , Al^{3+} , Ti^{4+} and Fe^{3+} . Basaltic glass dissolution is dependent on the Si content present in the glass. Higher

Si content causes a higher degree of polymerization and therefore, decreases the rate of dissolution substantially of both network-forming and modifying cations. This observation is important in that if the Type 2 terrain on Mars contains a primary high-silica glass component [18], element mobility and susceptibility of that primary material to chemical weathering would be significantly less. Laboratory observations have shown a decrease by a factor of 2000 in basaltic glass dissolution rate by increasing SiO_2 content in the glass from 48.8 wt. % to 57.8 wt. % [19]. The non-stoichiometric release of network modifying elements forms a residual leached layer, rich in structural silica and aluminum, which is destroyed at a much slower rate.

Feldspars, pyroxenes and basaltic glass have significantly different rates of dissolution and if this dissolution is non-stoichiometric, often form leached layers at the surface, rich in residual structural silica and aluminum, which are both relatively insoluble in acidic fluids. The presence of this leached layer is therefore common with basalt alteration and may also be a common process on Mars. Upon fluid evaporation, a process common among most models of soil formation on Mars, the thickest leached layers formed in our experiments craze and spallate. This may be important in that the leached layers may be released in to the Martian sediment and be redistributed as essentially amorphous silica, exposing fresh mineral and glass surfaces to alter. The reactivity of such a leached layer has been documented in that the pH of pore waters in this layer have a substantially higher pH than the bulk solution, which is conducive to precipitation of secondary phases inside the depleted layer [20]. Also, it may easily acquire negative surface charge and cause adsorption of aqueous constituents on to this layer [20]. Finally, the leached layer may also recombine and polymerize to form small amounts of phases such as clays, if enough aqueous constituents are available in the fluid [20].

Controls on fluid chemistry: Using basaltic compositions relevant to Mars, we observe that primary mineral phases each control different aspects of fluid chemistry. For example, Na^+ , K^+ and Ca^{2+} are ubiquitous in initial fluid compositions, due to their soluble nature and their weaker bonding in feldspars, pyroxenes and basaltic glass. The chemistry of Mg in these fluids is more complex. For example, forsteritic olivine is observed to dissolve the quickest in synthetic basalt alteration experiments, releasing large amounts Mg^{2+} and H_4SiO_4^0 into solution. This in turn raises the state of saturation with respect to amorphous silica as well as Mg- SO_4 phases, if fluids are rich in SO_4^{2-} . Magnesium from pyroxenes, however, may be released but kinetically inhibited, due to its preferential

M1 site occupancy and stronger bonding characteristics. Magnesium rich pyroxenes, such as enstatite, may be able to release significant amounts of Mg from the M2 site. This release is most likely limited to the first stages of alteration, in that a silica-rich depleted layer may soon form to retard dissolution. Therefore, in kinetically restricted models of alteration, olivine may be controlling the Mg^{2+} in the fluid as opposed to pyroxenes. Ferrous iron may also behave in this way, but results from synthetic basalt alteration experiments show that Fe^{2+} release from pyroxenes is much more significant than Mg^{2+} release in initial stages of alteration. With large amounts of Fe^{2+} being released into solution from pyroxenes and olivine, the fate of Fe^{2+} in solution remains uncertain because Fe^{2+} oxidation mechanisms are unconstrained. There are several pathways by which Fe^{2+} could be oxidized and in our synthetic alteration experiments exposed to the Earth's atmosphere, oxygen is the most important oxidant, producing secondary ferric phases as grains and coatings. More studies remain to be done to determine potential oxidants of Fe^{2+} on the Martian surface. Solid state iron oxidation of ferrous silicates and oxides [21] remains another possible mechanism for production of secondary ferric phases on Mars, but has been largely unexplored in this context.

Precipitation: The precipitation of minerals from various fluids depends on several factors. Among the most important factors observed in our experiments are the saturation state of the alteration mineral and the structure of both the precipitating mineral as well as the substrate on which it precipitates. Several experiments performed with synthetic basalt have shown large amounts of poorly crystalline alteration minerals precipitating on the surfaces of minerals and glasses. The initial phases are metastable or amorphous phases, which most likely have a higher rate of nucleation than subsequent stable phases, due to their wide-spread occurrence and poor crystallinity [22]. This process is referred to as Ostwald ripening and models such as palagonitization are dependent on such a process [2]. For example, the initial alteration phases precipitated during the formation of palagonite will most likely be metastable with respect to common alteration materials such as smectites observed in more advanced aging of palagonite.

Conclusions: Models for formation of the Martian soil share common fundamental aqueous processes, which are dependent on several factors prevailing on the surface. It is important to understand what these processes are and how they may be important during low temperature aqueous alteration. Several of these alteration processes begin with dissolution of primary mineral phases and are dependent on the chemistry of

the minerals themselves. Therefore, when testing models of low temperature aqueous alteration on Mars, relevant starting material is one of the most important factors. A wide variety of robust, analytical resources are also needed to characterize the chemical processes operating in laboratory systems, because microscopic observations in many cases, have global implications.

The discussion presented here is the result of the first stage of a large-scale approach to understanding the surficial processes on Mars experimentally. Many questions have been raised in light of recent observations and therefore, much work is needed to place further constraints on the origin of the Martian soil. More models for soil formation will be tested using even more starting materials, aqueous environments and experimental and analytical methods. The capability of synthesizing compositionally accurate starting material as well as adjusting experimental and analytical methods accordingly will result in observations aimed at a wide variety of microscale and macroscale processes that may be of importance for the surface of Mars. New constraints from future missions of Martian exploration will be used in our approach in further refining our understanding of the Martian surface material.

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