JUVENILE CHEMICAL SEDIMENTS AND THE DURATION OF AQUEOUS ACTIVITY ON ANCIENT MARS. N. J. Tosca[1] and A. H. Knoll[1], [1]Dept. of Organismic and Evolutionary Biology, Harvard University, 26 Oxford St., Cambridge, MA 02138 USA; ntosca@fas.harvard.edu

Introduction: Recent orbital and landed exploration has painted a complex geochemical picture of the earliest martian surface. It is clear that that water was at times present on early Mars, but it is the chemistry and persistence of that water that influences habitability [1]. Chemically benign conditions appear to surround carbonate and clay-bearing assemblages, while saline minerals reflect a harsher chemical environment before liquid surface water was permanently lost [2,3]. Aside from chemistry, even more basic is the requirement that liquid water persist long enough to mediate any first chemical steps toward life. But despite the seemingly disparate chemical environments indicated by aqueous minerals, almost all of the aqueous mineralogy identified on Mars reflects the consequences of an ancient surface that saw liquid water in episodes that lasted for only a geologic instant. Characterizing the habitability of the early martian waters is now as much a question of timing and duration as it is of chemistry.

Here we discuss mineralogical evidence for geologically brief episodes of liquid water on early Mars and a general lack of diagenetic maturation after initial deposition. This evidence is consistent with recent studies of valley networks, drainage basins and impact crater degradation, all of which point to transient rather than persistent liquid water on early Mars [4-7]. Such a martian surface may present an additional challenge for biology, but helps reconcile a number of difficulties associated with a protracted climate where liquid water persisted for significant geologic time.

Opaline silica and SiO_2 diagenesis: Silica is a common product when water interacts with mafic mineralogy [8], and there are numerous examples of its occurrence [8-11]. With time and available water, silica diagenesis progresses through opal-A, opal-CT, and finally, microcrystalline quartz [12-14]. Despite numerous examples of hydrated silica on Mars, there are no detections of quartz (the TES instrument should detect quartz at a level $\geq$ 5% [15]). One exception is the orbital detection of quartzo-feldspathic materials thought to be a result of igneous differentiation [16].

At the molecular level, liquid water drives the transformation of initially precipitated silica to less soluble polymorphs by dissolution-reprecipitation. This mechanism is supported by textural relationships, $^{18}O/^{16}O$ ratios, and thermodynamic and kinetic evidence [12-14]. For example, Williams et al. [12] have shown that the thermodynamic driving force behind the maturation of amorphous silica is the effect of surface area on solubility. This Ostwald Ripening process requires that initially amorphous silica will generally progress to cryptocrystalline or microcrystalline quartz if liquid water is present. On Earth, amorphous silica is uncommon in rocks that are more than a few million years old [17]; its persistence for billions of years at Gusev Crater, Meridiani Planum and a number of other localities suggests that water could not have persisted at these sites much beyond initial precipitation.

Basaltic weathering and clay-bearing assemblages: Mg/Fe-smectites (e.g., nontronite, saponite) dominate martian phyllosilicate assemblages. Al-rich clays, such as kaolinite, gibbsite and montmorillonite, are relatively rare [2]. Studies of clay mineral development in basaltic rocks as a function of annually averaged precipitation point to a common characteristic of smectite development on Earth – a significant dry season. For example, a study [18] focused on the mafic igneous rocks of the Sierra Nevada foothills showed that smectites were formed only in the driest climates, where gibbsite dominated the clay mineralogy in much wetter climates, with kaolinite representing a transition between the two (18; Fig. 1). A similar study [19] on clays developed on Hawaiian basalt as a function of drainage and precipitation yielded the same results; smectite developed on the dry side of the islands and gibbsite formed on the mountainous regions with heavy rainfall. Halloysite, generally associated with arid climate basaltic weathering [20], dominated assemblages produced from climates in between the extremes. These observations are also consistent with the clay mineralogy produced in low water-rock ratio closed-system basalt weathering experiments [21].

The comparison to clay mineral assemblages derived from terrestrial basalt indicates that the Mg/Fe-smectite assemblages found in various Noachian outcrops probably reflect a dry climate punctuated by episodes of aqueous activity. Although smectites are ubiquitous in most modern soils, exclusively smectitic soils on Earth rarely preserve in the geologic record [22]. This is mainly due to the relative stability of kaolinite versus smectite over geologic time; smectites become unstable in response to climate shifts from dry to progressively more humid environments.

Equally conspicuous is the persistence of smectite over billions of years without evidence of significant diagenetic transformation (e.g., chloritization or illitization) [23]. A limited K budget could be blamed for a lack of illitization among the dioctahedral smectites, but the reaction, as well as the chloritization of triocta-

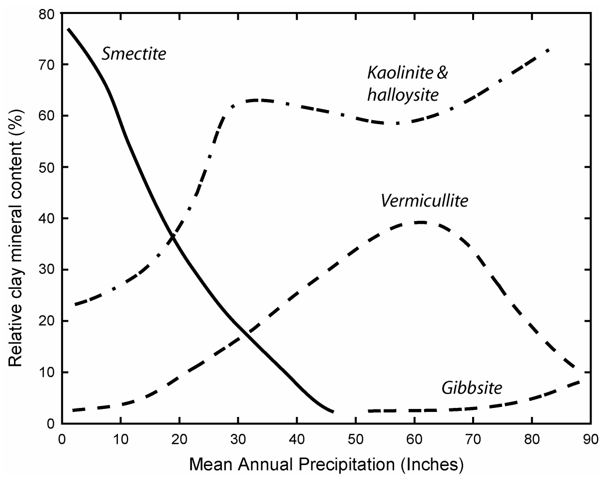

Figure 1. *Clay mineralogy developed from a basaltic host lithology as a function of annually-averaged precipitation (after Barshad, 1966).*

hedral smectites (arguably the dominant expected transformation on Mars), also requires liquid water. Time and burial history are both important in the transformation of smectites to illite and chlorite, but a detailed survey of Earth's geologic record shows that smectites older than 500 Ma are rare [24,25].

Fe-sulfates and oxides: The depositional environment recorded in Meridiani Planum evaporitic sandstones reflects a mostly subaerial environment punctuated by periods of groundwater infiltration [26]. Further, the persistence of jarosite argues for the limited duration of groundwater percolation during regional diagenesis [27]. The interaction of acidic water with a basaltic substrate will inevitably lead to an increase in pH through proton consumption and cation release. This, in turn, displaces the equilibrium saturation of Fe-sulfate minerals which require acidic pH. Thermodynamically, jarosite is metastable with respect to goethite and hematite; in water and over a range of pH, jarosite will transform to either of these phases depending on chemistry, pH and temperature within the sediment. Estimates of jarosite dissolution rates under various conditions indicate that, within errors typical of laboratory-derived dissolution rates, groundwater could not have persisted at Meridiani Planum for more than ca. 10^1 to 10^4 years [27]. Similar arguments can be made for other Fe-sulfates based on their thermodynamic stabilities, but less is known about the dissolution behavior of these minerals.

The persistence of aqueous activity and implications for habitability: Collectively, aqueous mineralogy reflects episodes in early martian history where water was available, but of geologically limited duration. The general lack of diagenetic maturation among aqueous sediments is consistent with the results of recent geomorphic studies that point to the limited and episodic appearance of water on early Mars with a sharp cessesion in fluvial activity around the late Noachian [4-7]. The exact nature of a wet Noachian climate, whether persistently wet or mostly dry, is not fully constrained. For example, a recent hypothesis for immature martian valley network development (compared to any found on Earth) argues for an extremely dry climate, with the Atacama desert being the only suitable Earth analog [5].

The implications for short-lived aqueous activity on the ancient martian surface could have influenced habitability in a significant way. Although some microorganisms can survive episodic dryness for prolonged periods of time, their persistence requires water to return on a regular basis between dormant states [28]. Nevertheless, the maximum lengths of dormancy and mechanisms responsible are still poorly known [28].

In total, mineralogical and geomorphic evidence for water on the early martian surface encompasses a small fraction of martian time. If surface water was available only intermittently and then vanished permanently, habitability of martian surface waters may have been affected by inadequate time for origination in, or adaption to chronically dry and/or potentially salty conditions before planetary water loss and significant climate change. Nevertheless, understanding the duration and timing of martian waters, in combination with their chemistry, will paint a more complete picture of habitability on ancient Mars.

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