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Juvenile Chemical Sediments and the Long Term Persistence of Water at the Surface of Mars

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Abstract

Chemical sediments and the aqueous alteration products of volcanic rocks clearly indicate the presence of water, at least episodically, at the martian surface. Compared to similar materials formed on the early Earth, however, martian deposits are juvenile, or diagenetically under-developed. Here we examine the role of water in facilitating various diagenetic reactions and evaluate the predicted effects of time and temperature for aqueous diagenesis on Mars. Using kinetic formulations based on terrestrial sedimentary geology, we quantify the integrated effects of time and temperature for a range of possible burial and thermal histories of precipitated minerals on Mars. From this, we estimate thresholds beyond which these precipitates should have been converted to the point of non-detection in the presence of water. Surface water has been shown to be at least episodically present in recent times. Nonetheless, the integrated duration of aqueous activity recorded over geologically long intervals by hydrated amorphous silica, smectite clays and Fe-sulfate minerals suggest that where these minerals occur water did not persist much beyond their initial deposition. This geochemical conclusion converges with geomorphologic studies that suggest water limitation during the late Noachian-Hesperian peak of valley formation and a still more limited footprint of water since that time. In addition to documenting the presence of water and its chemical properties, a complete assessment of

28   potentially habitable environments on Mars should address the timescales on which liquid water

29   has persisted and the timing of aqueous episodes relative to major planetary events.

30

31   *Keywords:* Mars, water, life, silica, clay, sulfate

32

33   **1. Introduction**

34   Liquid water undoubtedly left its mineralogical mark on the ancient martian surface.

35   Hydrated silicates (including clays), sulfates and (hydr)oxides occur in exposures of Noachian

36   and Hesperian age (~4.2-2.0 Ga; Ga: billion years), reflecting both spatial and temporal variation

37   in acidity, volatile content and redox state (Ehlmann et al., 2008a; Milliken et al., 2008; Mustard

38   et al., 2008; Squyres et al., 2008). Questions of habitability, however, require that we go beyond

39   simple presence/absence to investigate the chemistry and persistence of that water. Chemically

40   benign conditions appear to surround carbonate and clay-bearing assemblages (Ehlmann et al.,

41   2008a; Mustard et al., 2008), while saline minerals reflect a harsher chemical environment before

42   liquid surface water was largely lost (Tosca et al., 2008).

43   Perhaps the most basic requirement for habitability is that liquid water persist long

44   enough to mediate chemical evolution and sustain life once it arises. Here we discuss

45   mineralogical evidence for a general lack of diagenetic maturation among chemical sediments on

46   Mars. Juvenile precipitates – that is, precipitates that have undergone little diagenetic

47   modification since formation -- identified from outcrop investigations and remote sensing appear

48   to have formed during geologically brief episodes of liquid water on early Mars.   The

49   observation that these precipitates have persisted to the present further suggests that they have

50   seen little liquid water *since* they formed.   This conclusion is consistent with recent studies of

51 valley networks, drainage basins and impact crater degradation, which independently point to

52 transient rather than persistent liquid water on early Mars and a declining geomorphic influence

53 of water thereafter (Stepinski and Stepinski, 2005; Fassett and Head, 2008a; Fassett and Head,

54 2008b; Barnhart et al., 2009; Som et al., 2009).

55

56 **2. Mineralogical evidence for juvenile chemical sediments**

57 *2.1 Opaline Silica*

58   Silica commonly forms when water interacts with mafic rocks (McLennan, 2003). The

59 relatively rapid dissolution of olivine, pyroxene and basaltic glass compared to other rock-

60 forming silicates means that a significant amount of aqueous silica will be liberated during

61 basaltic weathering. Consistent with this, opaline (hydrated, amorphous) silica has been

62 identified in a number of locations on Mars. For example, geochemical mass balance and mini-

63 TES analyses of evaporitic sedimentary rocks at Meridiani Planum show that the rocks contain

64 significant amounts of hydrated silica, locally as high as ~20 wt.% (McLennan et al., 2005;

65 Glotch et al., 2006). At Gusev Crater, opaline silica was identified in the Columbia Hills and

66 interpreted as the product of intense aqueous activity, possibly related to hydrothermal processes

67 (Squyres et al., 2008). Using orbital data, Milliken et al. (2008) identified opaline silica in the

68 visible/near infrared (vis/NIR) using data from the MRO CRISM instrument. These latter

69 deposits, many of which are associated with Fe-sulfates, are of Hesperian age and effectively

70 expand the spatial and potentially temporal occurrence of opaline silica on ancient Mars. Recent

71 data from the TES and THEMIS instruments further indicate large deposits of amorphous silica

72 in western Hellas Basin (Bandfield, 2008). And more recently, a form of "hydrated silica" has

73 been identified in Noachian terrains associated with detections of phyllosilicate minerals

74   (Mustard et al., 2008); these detections are, however, spectrally distinct from the opaline silica

75   deposits analyzed by Milliken et al. (2008). We refer to these phases as amorphous and

76   opaline/hydrated silica; as treated here, these include siliceous deposits in the form of coatings,

77   residual leachates, or phases precipitated from solution (which can contain a number of

78   compositional impurities).

79   On Earth, amorphous silica rarely persists through geologic time. Inevitably, diagenesis

80   results in the sequential production of opal-A, opal-CT, and, finally, microcrystalline quartz

81   (Williams et al., 1985). The critical material needed to direct this reaction series is liquid water.

82   At the molecular level, water drives the transformation of initially precipitated silica to less

83   soluble polymorphs by dissolution-reprecipitation (Williams and Crerar, 1985), a mechanism

84   supported by textural relationships among silica polymorphs, $^{18}O/^{16}O$ analyses, and both

85   thermodynamic and kinetic evidence (Williams and Crerar, 1985). This Ostwald Ripening

86   process indicates that initially amorphous silica will generally progress to cryptocrystalline or

87   microcrystalline quartz in the presence of liquid water. On Earth, amorphous silica is uncommon

88   in rocks more than several million years old (Maliva et al., 1989) because of (1) the rapid

89   reaction kinetics of silica diagenesis and (2) the accelerating effects of post-depositional burial

90   and heating characteristic of most sedimentary basins. Indeed, the oldest known amorphous silica

91   occurs in siliceous microfossils within deep sea muds and small nodules in New Zealand coals,

92   both of Cretaceous age; the common feature of these stratigraphic outliers is the encasement of

93   amorphous silica within sediments of unusually low permeability (Lawrence, 1993; Sykes and

94   Lindqvist, 1993; Ogawa and Kawata, 1998).

95   Why, then, should amorphous silica persist on Mars over billion year time scales? With

96   one exception, all known examples of free silica on Mars are hydrated and amorphous. The

4

97   exception is an orbital detection of quartzo-feldspathic materials thought to be a result of impact

98   differentiation processes, although this mechanism may not apply to the entire region (Bandfield,

99   2006). The TES instrument should detect quartz at a level above 5% (Bandfield, 2008), and,

100   although by definition quartz does not contain structural water, natural samples do (e.g., Aines et

101   al., 1984), and so detection (albeit difficult) could be possible with vis/NIR spectrometers such

102   as OMEGA and CRISM.

103   The preservation of opaline or amorphous silica for billions of years across a number of

104   localities at the ancient martian surface suggests that water could not have persisted at these sites

105   much beyond initial precipitation. Alternatively, the observed lack of diagenetic maturation

106   among silica-bearing sediments could be blamed on different styles of tectonism and

107   sedimentation between Earth and Mars, preventing martian sediments from experiencing Earth-

108   like post-depositional conditions. Siever (1983) presented a method by which the cumulative,

109   integrated effects of time and temperature on diagenesis can be quantified for sedimentary basins,

110   regardless of their burial and thermal histories. In the absence of plate tectonics for much of its

111   geologic history, most sedimentary basins on Mars formed from impacts (McLennan and

112   Grotzinger, 2008). In general then, the burial history of martian sediments is likely to reflect

113   cycles of burial and exhumation, with thermal history controlled principally by local geothermal

114   gradients. The geothermal gradient is in turn controlled by the thermal conductivity of bedrock

115   and sediment, as well as by heat flux, which, for Mars, is known to have reached a maximum

116   during the Noachian and subsequently declined (McGovern et al., 2002; Carr, 2007).

117   We begin by considering two endmember burial histories for Noachian and Hesperian

118   sediments: (1) early deep burial, with little subsequent exhumation until recently, and (2) the

119   maintenance of juvenile deposits near the martian surface for the majority of post-depositional

120   time. Figure 1 depicts these contrasting burial histories as a function of time and temperature.

121   The first case assumes rapid burial to 2 km depth and thermal control by a deteriorating heat flux

122   over time [specified by a function which fits heat flux as a function of age for various regions of

123   the martian crust; (McGovern et al., 2002)], whereas the second case assumes little to no burial

124   following deposition at or near the sediment/air interface. (In the second case, we assume near

125   isothermal behavior for all of post depositional time.) Integrating under these curves gives the

126   time-temperature integral (TTI) as a function of time, shown on Figure 2a, with a comparison to

127   data for Paleozoic strata in the Illinois Basin (Siever, 1983; Moore, 2000). For the case of opal-

128   CT conversion to quartz, we are interested in estimating a maximum threshold for conversion;

129   that is, a single value representing any combination of time and temperature that will result in the

130   complete (within detection levels) conversion of hydrated silica to quartz.

131   For Mars, maximum time would involve exposure to liquid water at 0°C or less, with no

132   heating. Where surface water is frozen, our current understanding of diagenetic mechanisms

133   predicts that the lack of a liquid water phase would prevent diagenetic reactions from proceeding.

134   Although the freezing point can be depressed by increasing salinity or acidity, the effects of high

135   ion concentrations (and, by inference, low water activity, or a_{H2O}) on both the rate and

136   mechanism of diagenetic reactions are largely unknown. High salinity and low a_{H2O} limit liquid

137   water's availability as a solvent, and so reaction rates could either be increased as a result of

138   water diffusion from the mineral phase to solution (in the case of silica diagenesis; Lasaga, 1998)

139   or decreased by a lack of available solvent water. Ion concentration per se may also play a role,

140   but like the effects of diffusion, this has not been quantified at high ionic strength. For these

141   reasons, we have chosen to estimate the TTI threshold for 0°C using: (1) observed siliceous

142   mineralogy in terrestrial sedimentary basins, and (2) kinetic formulations of the opal-CT to

143   quartz reaction.

144   Data from the Miocene Monterey Formation in California, which contains discrete zones

145   of opal-A, opal-CT and quartz, allow us to estimate the TTI threshold based on an empirical

146   burial history from initial amorphous silica deposition in a deep sea basin (Compton, 1991).

147   Using a known burial versus time curve (Compton, 1991), assuming initial deposition in 5°C

148   seawater, and utilizing $^{18}O/^{16}O$ quartz formation temperatures ($\leq 62^{\circ}$C) for the Monterey

149   Formation to set both lower and upper temperature limits for diagenesis (Matheney and Knauth,

150   1993), we arrive at a TTI threshold of about $0.4\text{x}10^3$ Ma·$^{\circ}$C. This value can be obtained either by

151   integrating an extended polynomial function fit to the time-temperature curve (constructed from

152   burial and temperature limits), or by simple integration by Riemann sums. For our martian case 2

153   (no deep burial, 0°C), the equivalent time/temperature threshold would be reached after exposure

154   to water for about 400 Ma. A significant body of literature suggests that the kinetic rate law for

155   the opal-CT to quartz reaction holds at low temperature ($<25^{\circ}$C) because it involves dissolution

156   and reprecipitation reactions; the transition is known to occur at low temperature in a number of

157   terrestrial settings (Williams and Crerar, 1985; Williams et al., 1985; Botz and Bohrmann, 1991;

158   Matheney and Knauth, 1993).

159   As an alternative to geologically based estimates, we can estimate the conversion

160   thresholds using kinetic rate laws. For amorphous silica to quartz, conversion rates have been

161   estimated from experimental data collected at 300-500°C (Ernst and Calvert, 1969), but

162   extrapolating a high temperature rate law to low temperature by means of the Arrhenius

163   relationship is not valid for the silica-water system. Both Lasaga (1998) and Dove (1995) stress

164   that the differences in activation energies, or temperature dependencies, derived for silica-water

165   reaction kinetics depend on the temperature range of investigation. Higher activation energies are

166   associated with higher temperatures, where the faster process dominates the kinetics. Lasaga

167   (1998) compared the activation energies for quartz dissolution derived by Dove and Crerar (1990)

168   (19 kcal/mol at 200-300°C) and Casey et al. (1990) (8.4 kcal/mol at 30-70°C). The temperature at

169   which the rates are equal and temperature dependencies "cross over" is 54°C. This means that for

170   temperatures of 54°C and lower, there is a much lower temperature dependence on the quartz

171   dissolution rate. Thus, extrapolation of the opal-CT to quartz reaction from very high to low

172   temperature grossly overestimates the required time for conversion. Perhaps by coincidence,

173   conversion times at ~70-25°C are of the same order as natural observations, but the temperature

174   dependence of the reaction is likely erroneous. A more realistic way to estimate opal-CT

175   conversion would be to apply Casey et al. (1990)'s temperature dependence for low temperature

176   silica reactions to the 25°C opal conversion rate (based on high temperature kinetics) and then

177   estimate the time required where liquid water at the martian surface was always at 0°C. The

178   estimate yields 330 Ma for total conversion of opal-CT to quartz at 0°C, in reasonable agreement

179   with TTI thresholds from the Monterey Formation. Although the kinetically-based estimate

180   suffers from a lack of low temperature experimental data, it is likely to err in being too high –

181   applying the low-temperature activation energy to high-temperature-based estimates above 25°C

182   would result in shorter conversion times. Continued extrapolation of this relationship to

183   temperatures below 0°C would extend even further beyond experimental and theoretical support.

184   Aside from greater uncertainties associated with further temperature extrapolation, the extended

185   presence of liquid water below 0°C also requires knowledge of brine chemistry, introducing

186   further uncertainty, as discussed above. Nonetheless, if we assume that diagenetic reaction rates

187   below 0°C decrease proportionally with temperature, then they must also decrease in proportion

188   to increasing salinity (and decreasing water activity, a_{H2O}). Of course, the larger question is

189   whether such cold saline fluids would have been habitable; that is, would the potential extension

190   of habitability conferred by freezing point depression be countered by ice formation and low

191   water activity? A recent examination of saline mineral parent waters on Mars suggests that this

192   possibility must be taken seriously (Tosca et al., 2008).

193   In summary, geological and kinetic data agree that, even at low temperatures, opal-CT

194   conversion takes place on geologically rapid timescales. Indeed, as noted above, amorphous

195   silica, whether opal-A or opal-CT, is rare in rocks older than a few million years (Maliva et al.,

196   1989). The paucity of amorphous silica older than ~145 Ma in terrestrial rocks independently

197   suggests that our estimates for TTI thresholds for opal-CT to quartz conversion are realistic

198   maxima (Fig. 2b).

199   For both martian post-depositional models, complete conversion to quartz occurs early;

200   the maximum threshold is surpassed in less than 100-400 Ma (Figure 2b). Simply put, when

201   water is present, precipitated opal-A or opal-CT that remains at or near a cold ($0\,^{o}C$) martian

202   surface converts completely to quartz in approximately 300-400 million years. Importantly,

203   whether water was present intermittently (e.g., with episodic absence by evaporation or freezing)

204   or continuously, our calculations are representative of *the total contact time* between a liquid

205   water phase and a given mineral after its formation. A number of factors might accelerate or

206   hinder the reaction progress of opal-CT conversion. Pressure, for example, will accelerate

207   conversion, as will any chemical process that removes $H_4SiO_4^0$ from the aqueous phase (e.g.,

208   complexation, adsorption, clay mineral formation) (Williams et al., 1985; Hinman, 1998; Huang,

209   2003). Alternatively, the reaction may be slowed by any "deactivation" of the reacting silica

210   surface (e.g., by Fe adsorption; Dove, 1995). Regardless of these second order influences,

211 however, liquid water is undoubtedly the catalyst for silica diagenesis. The persistence of

212 amorphous silica on billion year time scales in Martian sediments suggests, parsimoniously, that

213 these widespread deposits have seen very little water since deposition.

214

215 *2.2 Smectite Clays*

216   Clays comprise another important class of surface minerals on Mars. In general, Mg/Fe-

217 smectites (e.g., nontronite, saponite) dominate martian phyllosilicate assemblages. In contrast,

218 Al-rich clays, such as kaolinite, gibbsite and montmorillonite, are relatively rare (Mustard et al.,

219 2008). A first-order comparison to clay mineral assemblages derived from terrestrial basalt

220 indicates that the Mg/Fe-smectites found in numerous Noachian outcrops probably reflect a dry

221 climate punctuated by episodes of aqueous activity. Although smectites are ubiquitous in most

222 modern soils, exclusively smectitic soils on Earth rarely preserve in the geologic record.

223   The main reason why smectites don't preserve is that they transform diagenetically to

224 more stable phyllosilicates (Weaver, 1989). The conversion of smectite into either illite (from

225 dioctahedral smectite) or chlorite (from trioctahedral smectite) through burial diagenesis and/or

226 metamorphism requires liquid water (Whitney, 1990; Altaner and Ylagan, 1997; Robinson et al.,

227 2002). A recent examination of chloritization reaction pathways indicates that the fluid to rock

228 ratio is key to reaction progress (Robinson et al., 2002).

229   At the molecular level, the hydration of cations to and from smectite,

230 dissolution/reprecipitation of smectite/illite layers, and the introduction of excess OH^- (in

231 chloritization) show that the reaction may not progress unless water is present (Whitney, 1990;

232 Altaner and Ylagan, 1997; Robinson et al., 2002). Perhaps the most convincing evidence for

233 water's role in catalyzing smectite conversion comes from experiments on the illitization of

10

234   smectite as a function of rock:water ratio (Whitney, 1990): the extent of illitization decreased

235   significantly with decreasing amounts of water. This inhibiting effect is most simply explained

236   by diffusion limitation. Decreasing water content leads to a greater fraction of unsaturated

237   porosity (i.e., wetted clay particles). As a result, the diffusion of ionic species to and from

238   smectite becomes increasingly controlled by surface diffusion, which is slow (Whitney, 1990;

239   Lasaga, 1998). Surface diffusion rates eventually become limited by increasing tortuosity and the

240   decreasing chemical gradient between solution and mineral, as solute concentrations build in the

241   fluid (Whitney, 1990; Lasaga, 1998). Diffusion across clay-bound water (i.e., at surfaces and

242   within interlayers), however, is only exacerbated by water's highly ordered nature, mainly from

243   electrostatic interactions (Sposito and Prost, 1982; Greathouse et al., 2000). In fact, for clays,

244   diffusion constants through surface and interlayer water have been estimated with molecular

245   dynamic simulations and are only a fraction of the bulk water value (Greathouse et al., 2000).

246   Smectite conversion is known to proceed under the effects of both temperature and time;

247   on Earth, discrete smectite (or illite/smectite with >5-10% smectitic layers) is rare in successions

248   older than ~600 Ma (Weaver, 1989). Returning to the time-temperature integral (TTI), it is

249   desirable to estimate TTI thresholds beyond which illitization would render smectite

250   undetectable on Mars. Again, estimates can be made using observed clay mineralogy in

251   terrestrial sedimentary basins and kinetic formulations of the smectite-illite reaction. For the

252   former, we focus our attention on terrestrial sedimentary basins where post-depositional thermal

253   history is well constrained. One of the best examples comes from studies of the Illinois Basin. In

254   particular, the Purington Shale (Pennsylvanian; ~310 Ma), buried to <1km and heated to no more

255   than $60^{o}C$, preserves <10% smectitic layers in diagenetic illite/smectite (I/S) (Moore, 2000). The

256   thermal history of this formation is well constrained, yielding time-temperature integral curves

257 (Figure 2; Moore, 2000) that provide a robust estimate for the illite-to-smectite threshold on

258 Earth or Mars. Based on the threshold value provided by the Purington Shale (Figure 2b), we

259 estimate that at 0^oC ~6 Ga are required to convert surface smectites to abundances below

260 detection limits.

261   Using reaction kinetics to estimate TTI thresholds for illitization is more difficult because

262 of the nature of the reaction mechanism. The temperature dependence of illitization has been

263 investigated experimentally and derived by fitting kinetic equations to illite/smectite mineralogy

264 in terrestrial sedimentary basins (Eberl and Hower, 1976; Bethke and Altaner, 1986; Velde and

265 Vasseur, 1992). As is the case for opal-CT conversion, high temperature experimental reaction

266 kinetics do not extrapolate well to low temperature. For illitization, however, they *under*estimate

267 the amount of time required for conversion, usually because smectite reacts more slowly as it

268 becomes progressively more illitic. A kinetic rate law introduced by Bethke and Altaner (1986)

269 takes this phenomenon into account and is consistent with illitization rates observed from a

270 number of basins. Adopting the same formulation and estimating the amount of time required to

271 convert smectite to >95% illite at 0^oC, this approach yields a time estimate of ~9.2 Ga. It is

272 difficult to know whether the illitization reaction will proceed at such a low temperature.

273 Nevertheless, this equation estimates ~180 Ma for conversion to 80% illite at 35^oC, which is in

274 good agreement with data suggesting that a maximum of 150 Ma was required to form 80% illite

275 under similar conditions from Lower Cambrian strata of the East European Platform (Kirsimae et

276 al., 1999).

277   We use TTI thresholds from both methods to establish maximum and minimum time

278 estimates for illitization on Mars, emphasizing that both estimates are consistent with

279 mineralogical and geological evidence on Earth and are equivalent to any combination of

12

280 temperature and time at the martian surface. The results show that burial or some other

281 modification of a near surface post-depositional environment is required to convert smectite to

282 illite (and/or chlorite) (Fig. 2b). It is well known that both illitization and chloritization occur at

283 low temperatures. Indeed, illite has been formed from smectite at room temperature in the

284 laboratory (Eberl et al., 1993) and at $<35^{\circ}C$ in unheated sedimentary basins (Kirsimae et al.,

285 1999); chloritization has also been documented at $<50^{\circ}C$ in natural settings (Walker, 1989; Eberl

286 et al., 1993). Kinetic data for the latter reaction are rare; however, chloritization involves many

287 of the same steps as illitization: the hydration and replacement of cations in octahedral and

288 interlayer positions and dissolution/reprecipitation steps (Robinson et al., 2002). Thus, the

289 estimate of illitization rates in Figure 2b is equally representative of the chloritization reaction,

290 showing that even minimal and possibly brief burial could be enough to cross the threshold

291 beyond which smectite declines to undetectable levels.

292 The TTI thresholds shown in Figure 2b represent an idealized case; a number of factors

293 could either accelerate or hinder reaction progress. For example, pore fluid chemistry (e.g., pH,

294 K^+, Al^{3+} and $H_4SiO_4^0$) plays a significant role, as does the composition of the initial smectite

295 (Altaner and Ylagan, 1997; Meunier, 2005). The former point deserves underscoring. The

296 observed lack of illitization could conceivably be blamed, at least in part, on lower available K

297 concentration in waters arising from a basaltic source. Chloritization (arguably the dominant

298 transition resulting from burial of trioctahedral smectites on Mars) does not require K, however;

299 and both reactions first require water.

300 The majority of phyllosilicates detected on Mars occur in rocks originally buried beneath

301 a substantial stratigraphic cover; in some cases, an overburden as thick as 4-5 km was present for

302 much of their post-depositional history (Mustard et al., 2008). Figure 3 shows the TTI curves for

303 smectite conversion as a function of initial burial depth. The burial and heat flux is the same

304 function as specified in Figure 1, but with the added constraint that as soon as a decay in global

305 heat flux brings shallow sediments back to surface temperature (i.e., 0°C), the TTI curve

306 increases linearly with time. This analysis indicates that, at burial depths of 300m or greater (and

307 a continuous surface temperature of 0°C), smectite deposited 3.5 Ga would have converted to

308 illite before the Hesperian ended. In addition, the *x*-axis on Figure 3 can be expanded to estimate

309 how long after initial formation smectites could be expected to convert as a function of burial

310 depth in the presence of water (Figure 4). The exact conversion times depend on rates of

311 sedimentation and burial, which, for the Noachian, may have been rapid, given denudation rates

312 inferred for this time (Hynek and Phillips, 2001). Importantly, local geothermal gradient will also

313 influence absolute conversion times. As discussed above, we can estimate the loss of primordial

314 crustal heat over time using estimates of crustal thickness from Mars Global Surveyor (e.g., the

315 shape of segment 3 shown in Fig. 1; McGovern et al., 2002), but detailed regional analyses of the

316 geothermal gradient must await a complementary understanding of the composition and

317 evolution of the martian crust.

318 Sedimentary deposits at Holden Crater, as well as the Eberswalde and Jezero fluvial

319 systems, all include smectite-dominated units that were buried to a minimum of a few hundred

320 meters following late Noachian/early Hesperian deposition (Ehlmann et al., 2008b; Grant et al.,

321 2008). In addition, Fe/Mg-smectites dominate stratigraphy at the bottom of the Noachian-

322 Hesperian Mawrth Vallis outflow channel, at a stratigraphic depth of approximately 600-700m

323 (Wray et al., 2008). At Nili Fossae, a smectite-rich basement unit is overlain by olivine-rich

324 deposits, which are in turn overlain by Syrtis Major lavas (Mangold et al., 2007). The

325 emplacement of these Hesperian volcanic units very likely exposed the underlying clay-rich units

326 to elevated temperatures, yet smectite remains the dominant clay. In comparison to Earth's

327 geologic record, where even the most benign post-depositional conditions have transformed

328 smectite older than ~600 Ma (Weaver, 1989), the persistence of smectite minerals on Mars is

329 striking.

330   Although the detection of more stable clay minerals (i.e., chlorite, illite, prehnite) has

331 been reported for some localities on Mars (Mustard et al., 2008), diagenesis/metamorphism is

332 only one of several potential mechanisms for their formation. In fact, these minerals may have

333 formed largely by impact-related hydrothermal processes, especially if their formation age is

334 contemporaneous with the large impact basins that covered ~43% of the martian surface during

335 late heavy bombardment (Frey, 2008). If minerals such as chlorite are in fact a major component

336 of martian clay mineralogy and we assume that they are exclusively the products of smectite

337 diagenesis/metamorphism, they must be reconciled with the dominance and persistence of

338 diagenetically immature smectites for billions of years at burial depths greater than a few

339 hundred meters, pointing to a conspicuous lack of diagenetic maturation. In other words, our

340 conclusions are based not on a lack of stable phases, but the persistence of their unstable

341 precursors. And because liquid water is known to catalyze the transformation of smectite through

342 cation hydrolysis and dissolution/reprecipitation, we once again conclude that a lack of post-

343 depositional water hindered diagenetic maturation.

344

345 *2.3 Fe-sulfate minerals*

346   At Meridiani Planum, late Noachian sandstones record the erosion of a salt-rich parent

347 lithology and subsequent, predominantly aeolian sedimentation, punctuated by intervals of

348 groundwater infiltration (Grotzinger et al., 2005; McLennan et al., 2005). The occurrence of Fe-

349   sulfate minerals throughout these sediments reflects a largely water-limited regime (Klingelhöfer

350   et al., 2004; Poulet et al., 2008; Dickson and Giblin, 2009). In particular, the presence of

351   abundant jarosite indicates a limited duration of groundwater percolation during diagenetic

352   episodes (Elwood Madden et al., 2004). Thermodynamically, jarosite is metastable with respect

353   to goethite and hematite; in water and over a range of pH, jarosite will transform to one or the

354   other of these phases depending on chemistry, pH and temperature conditions within the

355   sediment. Estimates of jarosite dissolution rates under various conditions indicate that, within

356   errors typical of laboratory-derived dissolution rates, groundwater could not have persisted at

357   Meridiani Planum for more than $\sim10^1$ to 10^4 years, a timescale consistent with jarosite's

358   disappearance from Rio Tinto terraces $\sim10^4$ years old (Elwood Madden et al., 2004; Fernandez-

359   Remolar et al., 2005; Smith et al., 2006). Similar arguments can be made for other Fe-sulfate

360   phases based on their relative thermodynamic stabilities, but less is known about the dissolution

361   behavior of these minerals.

362   At Meridiani Planum, the interaction of acidic water with a basaltic substrate would

363   inevitably have led to an increase in pH through proton consumption and cation release. This

364   would have displaced the equilibrium saturation of Fe-sulfate minerals (which are stable only at

365   low pH) and initiated their decomposition. Thus, their occurrence points to short-lived aqueous

366   episodes as a primary means of preservation. This line of evidence must also apply to other areas

367   of the martian surface where acidic water was present, but did not persist long enough for

368   increased pH (from basalt dissolution) to decompose the Fe-sulfates found in these localities.

369   Many of the same strata that contain opaline silica are thought to contain ferricopiapite, an Fe-

370   sulfate mineral which forms at pH on the order of 1 or less (Milliken et al., 2008). In addition,

371   Mössbauer and APXS analyses show that Fe-sulfate rich soils at Gusev Crater contain abundant

372   rhomboclase and/or ferricopiapite (Morris et al., 2006). Schwertmannite, an iron oxy-

373   hydroxysulfate, rapidly decomposes to either jarosite or goethite over a range of pH and so its

374   preservation on the martian surface could also indicate a water-limited history. Schwertmannite

375   is one of several plausible candidates for the "nanophase ferric-oxide" signature in Mössbauer

376   spectra of Meridiani sedimentary rocks, but unequivocal mineral identification has not been

377   possible using the analytical tools on the MER rover Opportunity (Klingelhöfer et al., 2004).

378   The Rio Tinto system in southwest Spain provides a suitable analog for examining the

379   end products of an acidic system dominated by Fe sulfates. Rio Tinto is distinct from other areas

380   on Earth that are affected by acid mine drainage because the acid sulfate system is generated

381   naturally from pyrite oxidation and has been operating for 1-2 million years (Fernandez-Remolar

382   et al., 2005). Fernandez-Remolar et al. (2005) analyzed the ferruginous terraces deposited in

383   areas adjacent to the modern river channel and drainage system. The terraces reflect the

384   deposition and diagenesis of initially acid sulfate minerals – curiously, they record unusual

385   "popcorn" sedimentary textures that are thought to reflect the initial deposition of Fe-sulfates

386   such as copiapite, the dominant mineral cycling Fe and acidity between wet and dry seasons

387   (Fernandez-Remolar et al., 2005). The mineralogy of the terraces as a function of age shows that

388   Fe-sulfates are a transient phenomenon - over time and in response to diagenesis, they transform

389   to goethite (of varying degrees of crystallinity and magnetic ordering) and, finally, hematite. The

390   terraces become dominated by goethite and hematite in ~10,000 years, but more precise age

391   constraints on the terraces are lacking (Fernandez-Remolar et al., 2005). Although the precise

392   amount of time required to transform these phases to more stable Fe-oxide counterparts depends

393   on pH, the transformation is rapid, explaining the disappearance of such unstable minerals from

394   terrestrial systems more than several tens of thousands of years old. On Mars, the preservation

395 of Fe-sulfates for 3.5 billion years points to water limitation over the vast interval since

396 deposition.

397

3. Discussion

399 *3.1 Water availability during deposition*

400 Without question, minerals exposed on the surface of Mars record the chemical action of

401 water at their time of formation. But these minerals further allow the possibility that water

402 availability was limited *during* sediment deposition, which we treat separately from the

403 continuing influence of water *following* deposition (discussed below).

404 Studies of clay formation in basaltic rocks as a function of annually averaged

405 precipitation point to a common characteristic of smectite development on Earth – a significant

406 dry season. For example, Barshad (1966) focused on the mafic igneous rocks of the Sierra

407 Nevada foothills, showing that smectites formed only in the driest climates. Gibbsite dominated

408 the clay mineralogy in much wetter climates, with kaolinite representing a transition between the

409 two. A similar study (Bates, 1960) on clays developed on Hawaiian basalt as a function of

410 drainage and precipitation yielded the same results; smectite developed on the dry side of the

411 islands while gibbsite formed in mountainous regions with heavy rainfall.

412 The development of Al-rich phyllosilicates from a basaltic lithology is dependent on a

413 number of parameters, of which precipitation and drainage are among the most important. On

414 Mars, Al-rich phyllosilicates are rare, and their spatially limited occurrence may actually be

415 more consistent with alteration of discrete ash beds rather than abrupt changes in hydrology or

416 climate. Pyroclastics tend to be composed mainly of glass, and this distinct difference in

417 crystallinity would have drastically affected their dissolution behavior and the aqueous activity

418   of Al^{3+} (Tosca et al., 2004; Wolff-Boenisch et al., 2004). Experiments, modeling and field

419   studies all show that the alteration of glassy material results in more efficient production of Al-

420   rich phases, without the significant leaching and aqueous throughput normally required to

421   produce Al-rich weathering profiles (e.g., Mirabella et al., 2005). An analysis of the clay

422   mineralogy and stratigraphy at Mawrth Vallis, one of the few areas where Al-rich clays have

423   been identified on Mars, shows that Al-bearing phases are confined to specific strata that drape

424   local topography, consistent with airfall pyroclastic deposition (Wray et al., 2008).

425   While currently available evidence does not rule out persistent water over significant

426   areas at the time of clay formation, little that has been observed requires it. Moreover, as noted

427   above, estimates of water duration based on clay mineralogy must be evaluated in the context of

428   observed sulfate and silica mineralogy. We conclude that in many locations on the early martian

429   surface, water was present episodically, but not persistently. Whether this was generally true of

430   Noachian Mars will be clarified by continuing studies of chlorite and illites that will tell us

431   whether these are primary mineral phases formed during hydrothermal alteration or mature

432   precipitates produced by diagenetic conversion of smectites.

433   One last point: although the amount of clay minerals present in martian rocks is

434   substantial (e.g., Mustard et al., 2008), the *abundance* of water at a given time on the martian

435   surface should be treated separately from its *persistence*, which we have focused on above.

436

437   *3.2 Post-depositional water availability*

438   The juvenile nature of hydrated amorphous silica, smectite clays and Fe-sulfates

439   collectively reflects limited water availability during the long interval from initial deposition to

440   the present. As argued above, water (on molecular, microscopic, and regional scales) is the

441   catalyst that drives the diagenetic maturation of sediments that were themselves initially formed

442   in water. Because the effects of water with time is an inescapable driving force in the maturation

443   and diagenesis of chemical sediments, these hydrated precipitates record the additive effects of

444   interaction with liquid water, whether continuous or episodic, since the time of their deposition.

445   There is abundant evidence to suggest that liquid water was at least episodically available

446   up until the very recent geologic past and perhaps even the present (Renno et al., 2009; Schon et

447   al., 2009); relatively young gully features have been identified from orbit, with at least one

448   example allowing age estimates from crater counting at ~1.25 Ma. One hypothesis is that these

449   geomorphologic features are the product of snow melting following orbitally-forced climate

450   excursions and so are repeatedly episodic but individually short-lived (Schon et al., 2009).

451   Although no chemical precipitates have yet been tied to these occurrences (perhaps again

452   suggesting their limited interaction with surrounding sediment), the story told by much older

453   chemical sediments suggests that the integrated effect of transient liquid water at the surface of

454   Mars for the past several billion years has not been enough to drive their diagenetic maturation.

455

456   *3.3 Supporting evidence from geomorphology*

457   Chemical and geomorphologic evidence are converging on a view of early Mars in which

458   water was present, but intermittently so. Modeling studies exploring the nature of Noachian

459   valley networks agree that an arid climate is required to reproduce the observed drainage

460   characteristics – a wetter climate invariably produces features inconsistent with observed

461   topographic distributions and branching patterns and causes breaching of craters where water

462   could have ponded (Stepinski and Stepinski, 2005; Barnhart et al., 2009; Som et al., 2009). The

463   exact nature of the "arid" Noachian climate remains contentious, however. Stepinski and

464   Stepinski (2005) argue that the closest Earth analogs come from the Atacama Desert, a region

465   with negligible annually averaged precipitation. They also suggest that some features, such as

466   catastrophic outflow channels, could be the result of repeated short-duration episodes of aqueous

467   activity. Another study on the origin of valley networks in the Parana Basin requires an arid to

468   semiarid climate that lasted for a minimum of 10^3-10^4 years (Barnhart et al., 2009). The authors

469   stress the importance of episodic precipitation events that must have been punctuated by periods

470   of evaporation to produce the observed morphologies. Recent orbital analyses are consistent with

471   this conclusion. Chloride-bearing mineral assemblages are spread across a significant fraction of

472   Noachian terrains, with a number of deposits on crater floors (Osterloo et al., 2008). Although

473   there is currently little additional mineralogical evidence for Noachian evaporation (as clay

474   minerals constrain pH but not salinity), subsequent aqueous episodes may have redistributed

475   soluble salts from insoluble phyllosilicates until the global cessation of aqueous activity where

476   extensive saline deposits, the last vestige of liquid water on the ancient martian surface, were

477   permanently deposited. Nevertheless, application of a new crater counting technique to 30 valley

478   networks showed that valley networks are concentrated around 3.7Ga, with abrupt

479   disappearance after this time (Fassett and Head, 2008a).

480   Morphologic evidence shows that water was present on early Mars and was perhaps

481   abundant enough to leave signs of an integrated subsurface hydrology (Fassett and Head, 2008b).

482   Yet the conspicuous lack of diagenetic maturation among chemical sediments and the estimated

483   times required to create fluvial features on the martian surface suggests that total duration was

484   limited to a small fraction of geologic time and that aqueous activity in the Noachian was

485   episodic. As an exercise, we can assume that all valley networks identified by Fassett and Head

486   (2008a) are of different ages and that each lasted for 1 million years (probably both

21

487   exaggerations). The collective valley network record would then occupy about 1% of Mars

488   surface history over the last 4.2 billion years. We note, as well, that evidence for liquid water in

489   recent Mars history does not by itself require that water have been continuously present for the

490   past several billion years. A model published by Richardson and Mischna (2005), for example,

491   suggests that the probability of liquid water at the martian surface could be higher today than it

492   has been for much of the planet's history. In continuing studies it will be important to place the

493   timing and duration of aqueous activity more firmly in the context of planetary history.

494

495   **4. The duration of aqueous episodes on early Mars and implications for life**

496   Short-lived aqueous activity on the ancient martian surface could have influenced

497   habitability in significant ways. We do not know how long it takes to form life from abiotic

498   precursors; neither do we understand how long organisms can survive in the absence of water. If

499   surface water was available only intermittently and then vanished permanently, habitability of

500   martian surface waters may have been affected by the limited time to originate in or adapt to

501   chronically dry and/or potentially salty conditions before planetary water loss and significant

502   climate change (Tosca et al., 2008).

503   If habitable environments did exist on early Mars, they are separated from Meridiani

504   Planum and younger intervals by late heavy bombardment (Frey, 2008), the termination of the

505   magnetic dynamo (Lillis et al., 2008), and associated atmospheric loss (Greenwood et al., 2008;

506   Tian et al., 2009). Tian et al. (2009) have suggested that in its earliest history Mars could not

507   have accumulated a thick CO_2 atmosphere because high EUV would have allowed C to escape

508   from the top of the atmosphere at high rates. Thus the "wet" martian interval may have been

509   relatively short, beginning as EUV waned and ending with the loss of a magnetic shield. During

510 late bombardment, impacts recorded by giant craters would likely have sterilized the planetary

511 surface (Sleep et al., 1989), with one of the last very large impacts, recorded by the ~1350 km

512 Isidis Basin, forming at ~3.8-3.9 Ga (Frey, 2008). Thus, arguments about post-Noachian life on

513 the martian surface require either that it originated *de novo* after late heavy bombardment in arid,

514 acidic, and oxidizing conditions that would challenge prebiotic chemistry (Gabel and

515 Ponnamperuma, 1967; Miller and Orgel, 1974; Tosca et al., 2008) or that it recolonized a

516 forbidding post-Noachian surface from an unspecified subsurface refugium. Unfortunately, the

517 sole example of life's origin does little to inform us of the necessary timescales for such a

518 process, in large part because of the uncertain origin of self-replicating molecular systems (such

519 as the so-called RNA world) which are thought to require a fortuitous combination of synthetic

520 events (Orgel, 1998).

521 Life on Earth emerged early in the history of a watery planet. Much interest in the

522 possibility that Mars also incubated living systems comes from the view that early in its history,

523 our red neighbor was more similar to Earth than it is today. While late Noachian-early Hesperian

524 Mars was certainly warmer and wetter than at present, evidence that it ever closely approximated

525 the Earth remains to be discovered. More likely, the context for astrobiological consideration of

526 Mars is an episodically wet planet that has been persistently dry for much of its history.

527

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715   deposits at Mawrth Vallis, Mars. Geophysical Research Letters 35(L12202): doi:

716   10.1029/2008GL034385.

717

718 **Figure Captions:**

719

720 **Figure 1:** Conceptual time-temperature curves for two end-members of sediment burial on Mars.

721 The solid line represents the evolution of a sediment package upon: (1.) burial to 2 km depth

722 under an estimated Noachian heat flux (80 mW m^{-2}) and thermal conductivity of 2.5 W m^{-1} K^{-1},

723 (2.) constant burial depth at constant Noachian heat flux, and (3.) constant burial depth at a

724 decreasing heat flux. The dashed line represents deposition at the surface and isothermal post-

725 depositional behavior.

726

727 **Figure 2: (A)** Time-temperature integral values as a function of post-depositional time for the

728 two end-member burial scenarios depicted in Figure 1, and for the Upper Cambrian and

729 Pennsylvanian of the Illinois Basin, for reference. **(B)** Time-temperature integral curves from (A)

730 with a change in the *y*-axis scale to show thresholds for opal-CT to quartz conversion and

731 smectite conversion to illite. Threshold values are shown as horizontal lines, representing any

732 combination of temperature and time needed to convert hydrated silica and smectite to non-

733 detection. Both end-member burial scenarios cross the opal-CT detection threshold soon after

734 formation, whereas some burial or heating is required for smectite to completely convert to illite.

735

736   **Figure 3:** Time-temperature integral curves as a function of depth and post-depositional time.

737   Using the burial, geothermal and heat flux functions specified in Fig, 1, models show that burial

738   depths of ~300m and greater would convert smectite to non-detection.

739

740   **Figure 4:** Time temperature integral curves as a function of depth and post-depositional time

741   (Figure 3, with a change in the *x*-axis scale). According to this burial scenario, smectite buried to

742   1000m would be converted to non-detection in ~480 Ma.