

24 carbonate outcrops on Mars using the reactive transport code CrunchFlow. Model inputs
25 included two parent rocks chosen based on the carbonate-rich rock at Gusev Crater,
26 Comanche, one consisting of 60% magnesite, 20% siderite and 20% porosity, and one
27 consisting of 50% magnesite, 20% siderite, 9% calcite, 1.6% rhodochrosite and 20%
28 porosity. Reacting solutions consisted of four scenarios: acidic, sulfate-containing
29 solutions, perhaps resulting from an acid vapor scenario; dilute solutions resulting from
30 martian analog basalt dissolution; concentrated solutions resulting from modeled
31 evaporation of the dilute solutions; and solutions based on the results of the Phoenix
32 Lander. Modeling was performed under low oxidation and high oxidation conditions.
33 Based on the modeling results, a carbonate rock would become enriched in siderite upon
34 interaction with acidic water under low oxidation conditions; the same rock would
35 become enriched in calcite after interaction with Ca-enriched solutions. A carbonate rock
36 reacting under more oxidizing conditions would preferentially dissolve siderite, leaving a
37 surface enriched in magnesite and ferric oxide. Therefore, the Mg-rich carbonates on
38 Mars are consistent with possible interaction with liquid water under oxidizing
39 conditions, similar to those measured at the Phoenix landing site. Future detailed
40 chemical and mineralogical profiles through weathered rock into the unaltered interior of
41 carbonate rocks may therefore allow the quantitative interpretation of the aqueous history
42 and possible habitability of locations on Mars.

43 Keywords: Mars, weathering, carbonates, siderite, calcite, reactive transport modeling,
44 dissolution, precipitation

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Introduction:

47 Water is a key component for life on Earth, and is considered a likely necessary
48 component for life on Mars. Therefore, the search for habitable environments on Mars
49 includes a search for environments altered by liquid water. Multiple mineralogies have
50 been used as indicators of martian environments that were likely altered by liquid water.
51 The iron oxide hematite was used as an indicator of likely interaction with liquid water at
52 the landing site of the Mars Exploration Rover Opportunity (Christensen et al., 2000);
53 similarly, clay minerals have been used as indicators of the climate history recorded at
54 Gale Crater, the landing site of the MSL Curiosity (Milliken et al., 2010). The mineral
55 olivine has been used to place constraints on liquid water on Mars (Stopar et al., 2006;
56 Olsen and Rimstidt, 2007; Hausrath et al., 2008a; Hausrath et al., 2008b), and jarosite on
57 the duration of liquid water at Meridiani Planum (Elwood Madden et al., 2009).
58 Carbonates both dissolve and precipitate at low pressures and temperatures and therefore
59 represent a key mineral indicator of potential water-rock interaction.

60 Several recent results document the presence of carbonates in multiple locations
61 on Mars. Results from the Mars Exploration Rover Spirit document Mg- and Fe-rich
62 carbonates present in outcrops at 16-34 wt % in Columbia Hills in Gusev Crater, Mars
63 (Morris et al., 2010). Similarly, CRISM data have been used to detect Mg-rich
64 carbonates in the Nili Fossae region (Ehlmann et al., 2008) and Ca- and Fe-rich
65 carbonates in Leighton Crater (Michalski and Niles, 2010). Pedogenic carbonates have
66 also been found by the Phoenix Lander in martian polar soils (Boynton et al., 2009;
67 Sutter et al., 2012). These recent observations are consistent with previous observations
68 of carbonates. Telescopic measurements suggested the presence of carbonates in
69 airborne dust and at the surface (Pollack et al., 1990; Calvin et al., 1994; Lellouch et al.,

70 2000), and thermal emission spectrometry measurements of dust are consistent with the
71 presence of Mg-rich carbonates at less than 5% (Bandfield et al., 2003; Hamilton et al.,
72 2005). Ca-, Mg- and Fe-rich carbonates, including calcite, dolomite-ankerite, and
73 magnesite-siderite have also been detected in martian meteorites (Mittlefehldt, 1994;
74 Harvey and McSween, 1996). Carbonates, which exist in multiple locations on Mars, are
75 therefore key potential mineral indicators of the aqueous history of those locations.

76 Observations of the martian surface provide important evidence of surface water
77 on Mars. Enrichments in S, Cl and Br, and apparent correlation of Mg with S suggest
78 mobilization and transport by water through the soil column exposed by the rover's
79 wheels in the Burroughs Subclass soils at Gusev Crater (Haskin et al., 2005; Wang et al.,
80 2006; Ming et al., 2008). Similarly, recent measurements of perchlorate at the Phoenix
81 landing site suggest transport of thin films of liquid water in the soil (Cull et al., 2010).
82 Pedogenesis has also been documented on Mars by Amundson et al. (2008) based on loss
83 of major rock-forming elements and addition of elements likely present as soluble salts.
84 Recent observations of recurring slope lineae appearing and lengthening also suggest the
85 presence of liquid brines currently present near the surface of Mars (McEwen et al.,
86 2011). Previous calculations suggest the possibility of liquid water in concentrated salt
87 solutions (Ingersoll, 1970), and in gullies and depressions where thin ice can be melted
88 by insolation (Hecht, 2002). In addition, carbon isotope measurements by the Mars
89 Phoenix spacecraft indicate strong influences by liquid water, suggesting low temperature
90 water-rock interaction occurring throughout martian history (Niles et al., 2010). Pre-
91 terrestrial Ca-carbonates are also present in a shergottite meteorite (Gooding et al., 1988).

115 The dissolution of carbonate minerals has been studied extensively e.g. (Sjoberg,
116 1976; Plummer et al., 1978; Busenberg and Plummer, 1982; Rickard and Sjoberg, 1983;
117 Sjoberg and Rickard, 1983; Chou et al., 1989; Schott et al., 1989; Alkattan et al., 1998;
118 Shiraki et al., 2000; Duckworth and Martin, 2003; Duckworth and Martin, 2004;
119 Arvidson et al., 2006; Jordan et al., 2007; Pokrovsky et al., 2009a; Pokrovsky et al.,
120 2009b). Here, in order to facilitate comparison between carbonate minerals of different
121 compositions, mineral dissolution rate laws were chosen from experiments that compared
122 two or more of the following carbonate minerals whenever possible: magnesite (Chou et
123 al., 1989), siderite (Duckworth and Martin, 2004), rhodochrosite (Duckworth and Martin,
124 2003), calcite (Chou et al., 1989), and dolomite (Chou et al., 1989). Rates are plotted
125 from the rate laws as the form

$$126 \quad R = k_{H^+} a_{H^+} + k_{H_2O} \quad , \quad (Eq. 1)$$

127 where R is the far from equilibrium rate ($\text{mol m}^{-2}\text{s}^{-1}$), k_{H^+} is the proton-promoted
128 dissolution rate constant, a_{H^+} is the activity of hydrogen ions, and k_{H_2O} is the dissolution
129 rate constant under neutral conditions. Carbon dioxide has been recently shown to have
130 only a minor effect on carbonate dissolution rates aside from its effect on pH (Pokrovsky
131 et al., 2009b), and a term for H_2CO_3 is therefore not included in these calculations. This
132 is a reasonable assumption at current martian CO_2 concentrations – CO_2 concentrations
133 may have been much higher and therefore more important on early Mars.

134 Rates of carbonate dissolution were calculated over a range of pH values (Figure
135 1). A comparison of these rates indicates that dissolution follows the order: calcite >
136 dolomite > rhodochrosite > siderite > magnesite. This order has been previously reported
137 and attributed to the rate of water molecule exchange in the hydration sphere of dissolved

138 cations in solution (Pokrovsky and Schott, 2002), a trend that has been noted for
139 carbonates and other mineral groups (Casey and Westrich, 1992). This suggests that,
140 although the exact mineralogy of the phases present on Mars is not known, this
141 relationship between cation chemistry and dissolution rate will likely be relevant to
142 carbonate weathering on Mars.

143 Precipitation rates for carbonates also vary strongly as a function of cation
144 identity. Inorganic carbonate precipitation rates, either measured or calculated to a
145 temperature range of ~ 25 ° C, have been published for a variety of minerals e.g.
146 (Romanek et al., 1992; Sternbeck, 1997; Jiménez-López et al., 2001; Jimenez-Lopez and
147 Romanek, 2004; Saldi et al., 2009), and results indicate that precipitation rates follow the
148 trend calcite > rhodochrosite > siderite > magnesite (Figure 2), with magnesite
149 precipitation kinetically inhibited at low temperatures (Saldi et al., 2009). This trend has
150 been documented previously, and decreasing precipitation rates attributed to the average
151 surface density charge of the cation surrounded by water molecules in solution
152 (Lippmann, 1973; Reddy and Wang, 1980; Mucci and Morse, 1983; Mucci, 1987;
153 Deleuze and Brantley, 1997). Therefore, although the exact carbonate phases are not
154 known on Mars, the trends in dissolution and precipitation described here are likely to be
155 relevant.

156 In order to test the types of signatures that might result from the interactions of
157 carbonate rocks with liquid water on Mars, we reacted two different carbonate rocks
158 corresponding to observed carbonate rocks on Mars (Morris et al., 2010) under scenarios
159 corresponding to possible aqueous alteration on Mars. Four possible aqueous scenarios
160 were modeled, including: initially dilute solutions resulting from dissolution of basalt

161 (Tosca et al., 2004); concentrated solutions of five different compositions (Tosca and
162 McLennan, 2006); acidic, sulfate-containing solutions, possibly corresponding to
163 solutions resulting from interaction of water with volcanic acidic aerosols such as under
164 acid vapor or acid fog conditions (Settle, 1979; Banin et al., 1997; Tosca et al., 2004;
165 Golden et al., 2005; Hausrath et al., in press); and solutions based on measurements by
166 the Phoenix lander (Boynton et al., 2009; Kounaves et al., 2009; Kounaves et al., 2010a;
167 Kounaves et al., 2010b; Quinn et al.). The pH of the dilute solutions was varied over a
168 range of possible pH values in order to test how dissolution and precipitation change as a
169 function of solution pH, while the acid vapor conditions and concentrated solutions were
170 tested under acidic conditions, and the solution based on Phoenix measurements under
171 alkaline conditions. The implications of these modeled alterations to observations of
172 Mars possible from orbiters and landers are then discussed.

173

174

Methods

175 *Model inputs:*

176 In order to interpret possible signatures of aqueous alteration on Mars, interaction
177 of Mars-relevant solutions with Mars-relevant carbonate rocks was modeled using
178 CrunchFlow. We made the following assumptions based on known compositions of
179 martian materials. We chose two compositions of carbonate rocks based on observations
180 from the Mars Exploration Rover Spirit (Morris et al., 2010). The first modeled rock
181 consists of (by volume) 50% magnesite, 20% siderite, 9% calcite, and 1.6%
182 rhodochrosite. This composition was chosen to allow the presence of Ca and Mn within
183 the carbonate rocks (Morris et al., 2010). The second modeled rock consisted of (by

184 volume) 60% magnesite and 20% siderite, which assumes the presence of only magnesite
185 and siderite in the parent carbonate rock, after Morris et al. (2010). In both cases, initial
186 porosity was assumed to be 20%, as a reasonable porosity for carbonate rocks (Moore,
187 2001). Secondary minerals allowed to precipitate included siderite, calcite,
188 rhodochrosite, magnesite, goethite and gypsum. Mixed-cation carbonates, including
189 dolomite, were not allowed to precipitate because of sparse kinetic data. Inorganic
190 dolomite precipitation is not common at low temperatures and is therefore not likely to
191 occur under martian weathering conditions (Arvidson and Mackenzie, 1999; Sanchez-
192 Roman et al., 2009). Model inputs, including mineral composition, surface area,
193 equilibrium constants, dissolution and precipitation rate constants, and activation energies
194 are presented in Table 1.

195 The total reactive surface area, the actual mineral surface area that reacts with
196 aqueous solutions, is difficult to constrain even in carefully controlled laboratory
197 experiments, and has been considered to be the largest source of uncertainty in terrestrial
198 field calculations of mineral dissolution rates (White, 2002). Reactive surface area may
199 be better approximated by geometric surface area based on the size of the particle than by
200 surface area measured by gas adsorption, as is common in laboratory experiments
201 (Gautier et al., 2001). During chemical weathering in natural environments, the mineral
202 surface actually in contact with weathering fluids is also difficult to determine, but may
203 be only 0.1 to 10% of the measurable surface area (Velbel, 1993).

204 In order to normalize the mineral dissolution rates to relevant surface areas,
205 therefore, we calculated surface roughness for carbonate minerals from BET-measured

206 surface areas and geometric surface areas from the literature (Plummer et al., 1978;
207 Pokrovsky and Schott, 1999; Duckworth and Martin, 2003; Pokrovsky et al., 2005):

$$208 \quad \lambda = \frac{A_{BET}}{A_{geo}} \quad (Eq. 2)$$

209 where λ is the dimensionless surface roughness, A_{BET} is the specific surface area in m^2/g
210 measured by gas adsorption, and A_{geo} is the geometric surface area calculated using the
211 equation

$$212 \quad A_{geo} = \frac{6V_m}{W_m D} \quad (Eq. 3)$$

213 where V_m is the molar volume in m^3/mol , W_m is the molar mass in g/mol , and D is the
214 grain diameter in m. These calculated surface roughnesses were multiplied by the
215 geometric surface area calculated for a hypothetical 1 mm spherical grain of each
216 carbonate mineral used in the model to obtain a mineral surface area for inclusion in the
217 model. The size of the 1 mm grain is based upon the scale of the surface roughness of the
218 carbonate rock observed by the Mars Exploration Rover Spirit (Morris et al., 2010),
219 which may result from dissolution.

220 Previous measurements indicate that, in terrestrial environments, 90-99.9% of the
221 available mineral surface area is likely not in contact with solution (Velbel, 1993). We
222 therefore assume that martian carbonates are likely to be in the lower range of wetted
223 surfaces and therefore decreased the specific surface area used in our calculations by
224 three orders of magnitude. Although these surface areas are approximations, they are
225 consistent with the assumptions listed above, and are sufficient to test a mineralogical
226 signature of aqueous alteration.

227 Aqueous transport consisted of diffusive transport, with a tortuosity of 0.5 (Saner
228 et al., 1996; Mair et al., 1999; Azar et al., 2008), an initial porosity of 20% (Moore 2001),
229 and 100% liquid saturation. Species specific diffusion coefficients taken from the
230 literature are corrected for temperature using an activation energy of 4.5 kcal/mol (Maher
231 et al., 2006). Electrochemical migration is also calculated within the model using the
232 Nernst-Planck equation (Giambalvo et al., 2002), which preserves electroneutrality.

233 Although abundant geomorphic evidence for liquid water exists on Mars e.g.
234 (Carr, 1996), the characteristics of that liquid water remain poorly constrained.
235 Therefore, we tested four different scenarios for the interaction of aqueous solutions with
236 carbonates. In Scenario 1, we reacted acidic water containing sulfate but no other cations
237 or anions with the carbonate rock, which may correspond to solutions resulting from
238 reaction of water with volcanic acidic aerosols such as under acid vapor or acid fog
239 conditions (Settle, 1979; Banin et al., 1997; Tosca et al., 2004; Golden et al., 2005;
240 Hausrath et al., in press). Scenario 2 used dilute solutions formed from the alteration of a
241 Mars-analog basalt. We chose cation concentrations after Tosca et al. (2004), except that
242 the Fe concentrations were reduced to zero and solutions contain sulfate (Table 2). Iron
243 concentrations in input solutions were reduced to zero to account for possible oxidation
244 and precipitation at the surface. In order to constrain the effects of solutions possibly
245 concentrated by evaporation, in Scenario 3, we used five more concentrated solutions
246 based on Tosca and McLennan (2006). Concentrated solutions, including brines, may
247 play or have played an important role on Mars (Brass, 1980; Knauth and Burt, 2002;
248 Sears and Chittenden, 2005; Tosca and McLennan, 2006; Zolotov and Mironenko,
249 2007b; Altheide et al., 2009; Elwood Madden et al., 2009; Hausrath and Brantley, 2010).

250 For each concentrated solution, the enriched cation concentrations were assumed to be
251 10x higher than the concentrations in Tosca et al. (2004), except that Fe was reduced as
252 described above. In Scenario 4, we used solutions based on measurements from the
253 Phoenix lander (Boynton et al., 2009; Kounaves et al., 2009; Kounaves et al., 2010a;
254 Kounaves et al., 2010b; Quinn et al.). Based on measurements from the Phoenix lander,
255 Ca, Mg and bicarbonate concentrations were assumed to be in equilibrium with calcite
256 and magnesite, and sulfate in equilibrium with gypsum. All equilibrium calculations
257 were performed in PhreeqC (Parkhurst and Appelo, 1999). K concentrations used were
258 the concentrations measured in the soil-solution slurries from Phoenix adjusted for 20%
259 porosity (Table 2) (Kounaves et al., 2010a). Within the model, solution compositions,
260 including pH, were updated for each cell at each time step as a result of geochemical
261 reactions including dissolution and precipitation, and activity coefficients are calculated
262 using the extended Debye-Huckel model.

263 To test the effect of oxidation, all modeling was performed under two oxidation
264 conditions. One, assumed to be a lower limit, was O₂ in equilibrium with atmospheric O₂
265 set to current concentrations on Mars. This condition might reflect less oxidizing soils or
266 conditions beneath the surface. For the other, more oxidizing condition, the aqueous O₂
267 concentration was set to 0.002625 mol, based on tests of materials corresponding to the
268 Phoenix results (Quinn et al., 2011), and assuming a porosity of 20%.

269 Temperature was set to 1° C, and pH varied. Scenario 2 was modeled at solution
270 pH values ranging from 2-8, while Scenarios 1, 3 and 4 were each modeled under one pH
271 condition (pH=2, 4 and 7.7 respectively). Pore water cation concentrations within the
272 carbonate rock were assumed to be in equilibrium with the carbonates, as calculated by

273 PhreeqC (Parkhurst and Appelo, 1999), except for Scenario 1, in which case they were
274 set to zero.

275

276 *Reactive transport modeling:*

277 Modeling was conceptualized as a one dimensional column of 100 cells
278 representing a carbonate outcrop, with a Dirichlet boundary for aqueous and gaseous
279 species at the rock-atmosphere surface, and a flux boundary at the base of the column.
280 Solution diffused from the top of the column to the base. The simulations use a global
281 implicit reactive transport approach (GIMRT) which solves transport and
282 multicomponent reactions simultaneously (Steefel and Lasaga, 1994; Steefel and
283 MacQuarrie, 1996).

284 We used parallel rate laws to incorporate the strong pH dependence of carbonate
285 dissolution (Table 1; Equation 1). In order to model the dependence on saturation state
286 for precipitation rates of each mineral, a separate precipitation rate law was incorporated,
287 using measured values for the dependence on the degree of supersaturation (m) from the
288 literature (Table 1). Models were run until the modeled weathering profile did not
289 change with additional time except for increasing weathering advance.

290 When convergence had been achieved after each time step, the mineral volume,
291 surface areas, and porosity were each updated within CrunchFlow. The total surface area
292 was updated according to a shrinking sphere model (Levenspiel, 1972; Lasaga, 1998;
293 Burkin, 2001). The total porosity (initially 20% as a reasonable approximation of a
294 carbonate rock (Moore, 2001)), is first calculated from the sum of the mineral volume
295 fractions input into the model (Table 1). In order to most realistically model the behavior

296 of the system, the model was set to the porosity_update option, such that the total
297 porosity was updated after each time step. The minimum porosity was set to 3%.

298

299

Results and Discussion

300 In order to test the prediction that reactions of carbonates with aqueous solutions
301 would result in chemical and mineralogical changes that could act as indicators of
302 aqueous interaction on Mars, we performed reactive transport modeling simulating
303 interaction of two Mars-relevant carbonate rocks with four types of Mars-relevant
304 aqueous solutions at a variety of pH values, under low oxidation conditions (in
305 equilibrium with atmospheric O₂) and high oxidation conditions (mmol concentrations of
306 O₂ in solution based on Phoenix solutions (Quinn et al., 2011)). Outputs of this reactive
307 transport modeling include parameters such as bulk chemistry and mineralogy, surface
308 area and porosity of the porous medium, gas concentrations, pore water chemistry and
309 speciation, pH, and the saturation state and dissolution and precipitation rates of the
310 minerals. To compare modeling results most directly to observations from Mars, the
311 volume of the minerals in the model output is plotted as a function of depth from the
312 original rock surface (Figures 3, 4, and 5). Results of the modeling are then compared
313 with observations from Mars to identify potential aqueous indicators.

314 Four aqueous scenarios were compared, Scenario 1, acidic aqueous solution
315 containing sulfate and no cations, possibly corresponding to solutions resulting from
316 interaction of water with volcanic acidic aerosols such as under acid vapor or acid fog
317 conditions (Settle, 1979; Banin et al., 1997; Tosca et al., 2004; Golden et al., 2005;
318 Hausrath et al., in press), Scenario 2, dilute solutions representing dissolution of a Mars-

319 analog basalt after Tosca et al. (2004), Scenario 3, solutions resulting from modeled
320 evaporation of solutions resulting from reaction of basalt after Tosca and McLennan
321 (2006), and Scenario 4, solution based on measurements by the Mars Lander Phoenix
322 (Boynton et al., 2009; Kounaves et al., 2009; Kounaves et al., 2010a; Kounaves et al.,
323 2010b; Quinn et al., 2011).

324 In each case, dissolution caused retreat of the original rock surface (Figures 3-5).
325 The overall retreat of the surface, the distance from the original surface of the rock to the
326 outermost mineral present after reaction, increased with decreasing pH of the initial fluid,
327 which was systematically varied for Scenario 2 (Figure 3). This trend is seen for both the
328 magnesite-siderite and the magnesite-siderite-calcite-rhodochrosite starting materials.

329 Although it may not be possible to identify the original surface of a reacted rock
330 in a natural system, other changes in the rock with dissolution often can be identified.
331 Differences in dissolution behavior of each mineral may cause a granular, pitted surface
332 of the rock, which is consistent with the observations of the carbonate outcrop by the
333 Mars Exploration Rover Spirit on Mars (Morris et al., 2010).

334 In addition to characteristic depths to reaction front, or weathering advance, the
335 change in the volume of minerals with depth varied characteristically between minerals
336 for both rock types. Siderite had a characteristically sharp front, often increasing from
337 close to zero to tens of percents over a small distance (Figure 3). In contrast, the increase
338 in percentage of calcite was often much more gradual (Figure 3). The change in the
339 volume of the minerals with depth as a function of weathering results in a weathering
340 profile that can be characterized in natural environments, and has been documented to
341 record the conditions of formation e.g. (Lichtner, 1988; Steefel et al., 1990; White, 2002;

342 Sak et al., 2004; Steefel et al., 2005; Hausrath et al., 2008a; Maher et al., 2009; Navarre-
343 Sitchler et al., 2009; Sak et al., 2010; Hausrath et al., 2011; Navarre-Sitchler et al., 2011).
344 The shape of a reaction front generally results from the relationship between dissolution
345 rate and rate of transport; when the dissolution rate is fast relative to transport, reaction
346 fronts are abrupt, and when transport is fast relative to dissolution, reaction fronts are
347 more gradual (Lichtner, 1988; White, 2002).

348 Precipitation of secondary carbonate minerals generally occurs under low
349 oxidation conditions (Figures 3 - 5). For the magnesite-siderite rock, siderite usually is
350 the only secondary mineral formed, precipitating in various amounts under different
351 aqueous conditions. Rhodochrosite and calcite also precipitated in the magnesite-
352 siderite-calcite-rhodochrosite rock under different pH conditions (Figure 3). When the
353 carbonate rocks are reacted with Ca-enriched solutions (Table 2), both calcite and siderite
354 precipitate (Figure 5). Under high oxidation conditions, siderite did not precipitate, and
355 in contrast, siderite dissolved rapidly, and goethite precipitated (Figure 4).

356 The precipitation of rhodochrosite and siderite replacing magnesite may be an
357 example of the common ion effect, whereby more soluble minerals are replaced by less
358 soluble minerals (Table 1). In contrast, calcite has much faster precipitation kinetics
359 (Figure 2, Table 1). In some cases under low oxidation conditions, goethite precipitated
360 in the outermost cell of the model (not plotted here). Under high oxidation conditions,
361 goethite replaced siderite.

362 The interaction between dissolution and precipitation of carbonates is
363 undoubtedly more complicated than that presented here. Modeling a natural system as a
364 mathematical problem requires many simplifications and assumptions, and if conditions

365 on Mars differ from those used in the model here, then observations from Mars could be
366 different from the results modeled here. Additionally, we here address a targeted
367 question (the interaction of carbonates with liquid water), rather than other related
368 processes such as evaporation. However, the use of reactive transport modeling allows
369 important predictions to be made of signatures resulting from carbonates interacting with
370 aqueous solutions on Mars.

371

372 **Comparison to observations from Mars and predictions regarding future**
373 **discoveries**

374 Our modeling results indicate that variation in carbonate composition under Mars-
375 relevant conditions can be a result of interaction of solutions with mixed carbonate rocks,
376 causing the precipitation of siderite, calcite, rhodochrosite and goethite. Interactions of
377 carbonate minerals with liquid water could therefore cause characteristic changes
378 observable from orbit. For example, a rock containing only magnesite and small amounts
379 of siderite after Morris et al. (2010), would become enriched in siderite upon interaction
380 with acidic water under low oxidation conditions, and calcite upon interaction with Ca-
381 enriched solutions. In contrast, rocks that had interacted under high oxidation conditions
382 would become preferentially enriched in Mg-rich carbonates due to dissolution of other
383 phases. Therefore, the surface of a rock that had interacted with liquid water under low
384 oxidation conditions would likely appear more Fe- or Ca-rich than the unaltered rock, and
385 observations of Mg-rich carbonates over the Mars surface are consistent with interaction
386 with solutions under high oxidation conditions.

387 Comparing the altered surface and near-surface characteristics of a rock with the
388 unaltered interior would be an excellent way to constrain aqueous alteration. This type of
389 comparison is possible when the altered surface has been removed by physical
390 weathering, or by drilling by landers. Weathering profiles through the weathered
391 surfaces of rocks on Mars into the unaltered interiors have been identified and interpreted
392 previously (Haskin et al., 2005; Hurowitz et al., 2006; Hausrath et al., 2008a). Detailed
393 chemical and mineralogical profiles through weathered surfaces into the unaltered
394 interior allow the relative comparison of mineral persistence within the profile, and allow
395 a quantitative interpretation of the aqueous history of those profiles. Future exploration
396 of Mars, including depth profiles into carbonate rocks to compare altered surfaces to
397 unaltered interiors, could allow quantification of the record of aqueous alteration and
398 possible habitability of those locations.

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- 721

722 **Figure Captions:**

723

- 724 Figure 1. Dissolution rates of calcite, dolomite, rhodochrosite, siderite, and magnesite,
725 calculated from published rate laws (Chou et al., 1989, Duckworth and Martin., 2003,

726 2004). Comparison suggests that dissolution rates on Mars would follow, as previously
727 documented (Pokrovsky and Schott, 2002), the order calcite > dolomite > rhodochrosite
728 > siderite > magnesite. The fast dissolution rates of carbonates may help provide
729 constraints on liquid water on the surface of Mars.

730

731 Figure 2. Precipitation rates of calcite, siderite, magnesite and rhodochrosite as a
732 function of saturation state (Romanek et al., 1992; Sternbeck, 1997; Jimenez-Lopez et al.,
733 2001; Jimenez-Lopez and Romanek, 2004 and Saldi et al., 2009). Precipitation rates
734 suggest that the likely precipitation order at 25 ° C is calcite> rhodochrosite> siderite >
735 magnesite.

736

737 Figure 3. Modelled mineral profiles through a hypothetical carbonate rock consisting of
738 magnesite, siderite, calcite and rhodochrosite after Morris et al. (2010) reacted with a
739 dilute solution resulting from reaction with basalt (Tosca et al., 2004) under low
740 oxidation conditions at a) pH = 2, time = 10 years b) pH = 4, time = 10 years c) pH = 6,
741 time = 500 years and d) pH = 8, time = 500 years. In each case a depth of zero indicates
742 the original surface of the rock, at time zero. The original porosity of the rock was 20%
743 volume. Enrichment and persistence of siderite appear to be important indicators of
744 aqueous alteration under low oxidation conditions.

745

746 Figure 4. Modeled mineral profiles through a hypothetical carbonate rock consisting of
747 magnesite, siderite, calcite and rhodochrosite after Morris et al. (2010) reacted with a
748 dilute solution resulting from reaction with basalt (Tosca et al. 2004) for 10 years at a)

749 pH = 8, under low oxidation conditions b) pH = 8, high oxidation conditions c) pH = 2,
750 low oxidation conditions and d) pH = 2, high oxidation conditions. In each case a depth
751 of zero indicates the original surface of the rock, at time zero. The original porosity of
752 the rock was equal to 20%. Results suggest that reaction of a magnesite- and siderite-
753 containing rock would be relatively enriched in magnesite and ferric oxide when reacted
754 with a high-oxygen solution due to dissolution of siderite, and in siderite when reacted
755 with a low-oxygen solution (such as beneath the land surface) due to precipitation of
756 siderite. Results are consistent with Mg-rich and Mg- and Fe-rich carbonates observed on
757 Mars.

758

759 Figure 5. Modelled mineral profiles resulting from interaction of Ca-enriched solutions
760 with hypothetical carbonate rocks after Morris et al. (2010) a) Scenario 3 solution III with
761 a 2-carbonate rock under low oxygen conditions b) Scenario 3 solution II with a 2-
762 carbonate rock under low oxygen conditions c) Scenario 3 solution III with a 4-carbonate
763 rock under low oxygen conditions and d) Scenario 3 solution II with a 4-carbonate rock
764 under low oxygen conditions. Results indicate the precipitation of siderite and calcite,
765 suggesting that enrichment in siderite and calcite could be indications of interaction with
766 Ca-containing solutions under low oxidation conditions. Solutions were based on
767 calculations by Tosca et al. (2006) indicating enrichment by evaporation.

768 Table 1. Input parameters for reactive transport modeling.

Mineral	Reaction stoichiometry	$\log k_{H^+diss}$ ($\text{mol m}^{-2} \text{s}^{-1}$)	n_{H^+}	$\log k_{H_2O}$ $_{diss}$ ($\text{mol m}^{-2} \text{s}^{-1}$)	$\log k_{pp}$	m	$\log K$ (298K) ^{§§j}	Initial volume fraction ^{††}	surface area (m^2/g)	Ae (kJ/mol)
Calcite	$\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$	-0.05 [*]	1 [*]	-6.18 [*]	1.66 [‡]	1.09 [‡]	1.8487	0/0.09	3.64×10^{-6}	48.2 [/]
Magnesite	$\text{MgCO}_3 + \text{H}^+ = \text{Mg}^{2+} + \text{HCO}_3^-$	-4.6 [*]	1 [*]	-9.34 [*]	-13.387	2	2.2936	0.6/0.5	9.17×10^{-6}	39.7 ^{//}
Siderite	$\text{FeCO}_3 + \text{H}^+ = \text{Fe}^{2+} + \text{HCO}_3^-$	-4.6 [#]	0.75 [#]	-8.65	-6.34 ^{**}	1.09 ^{**}	-0.192	0.2/0.2	6.15×10^{-5}	49.4 ^{§§}
Rhodochrosite	$\text{MnCO}_3 + \text{H}^+ = \text{Mn}^{2+} + \text{HCO}_3^-$	-4.93 [§]	0.5 [§]	-8.45 [§]	-3.25 ^{††}	1.724 ^{††}	-0.1928	0/0.016	1.62×10^{-6}	49.4 [«]
Goethite	$\text{FeOOH} + 3\text{H}^+ = \text{Fe}^{3+} + 2\text{H}_2\text{O}$			-7.94 [†]	TST ^{###}		0.5345	0	3.30×10^{-5}	86 [»]
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$			-2.79	TST ^{###}		-4.4823	0	3.30×10^{-5}	41.8 ^{///}

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770 ^{*}Chou et al. (1989)

771 [#]Duckworth and Martin (2004)

772 [§]Duckworth and Martin (2003)

773 [†]Ruan and Gilkes (1995)

774 [‡]Jimenez-Lopez et al. (2001)

775 ^{||}Saldi et al. (2009)

776 ** Siderite precipitation rate constant estimated from Jimenez-Lopez et al. (2001) and Jimenez-Lopez and Romanek (2004). m
777 estimated from Jimenez-Lopez et al. (2001).

778 †† Sternbeck (1997)

779 ## Transition State Theory

780 §§ Thermodynamic data from the database based on Lawrence Livermore National Laboratory thermodynamic modeling
781 (thermo.com.V8.R6).

782 ‡‡ Volume fraction from Morris et al. (2010), with the first value for the magnesite-siderite rock, and the second value for the
783 magnesite-siderite-calcite-rhodochrosite rock, with a porosity = 20%

784 || For calculation of reactive surface area of carbonates see text.

785 / Pokrovsky et al. (2009)

786 // value used = the mean of values from Pokrovsky et al. (2009) and Higgins et al. (2002)

787 §§ value used = the mean of values from Greenberg et al. (1992) and Golbeev et al. (2009)

788 « value used = value for siderite, as there were none found for rhodochrosite, and siderite and rhodochrosite have similar
789 dissolution rates

790 » Ruan and Gilkes (1995)

791 /// Liu and Nancollas (1971)

793 Table 2. Compositions for solutions modeled. Scenario 1 consists of acidic, sulfate-containing solution perhaps resulting from an
 794 acid vapor scenario (Settle, 1979; Banin et al., 1997; Tosca et al., 2004; Golden et al., 2005). Scenario 2 corresponds to a solution
 795 that would result from the weathering of a hypothetical martian basalt (Tosca et al., 2004). Scenario 3 corresponds to a series of
 796 solutions concentrated by evaporation that could result from aqueous interaction with a basalt (Tosca and McLennan, 2006), and
 797 Scenario 4 corresponds to solution based on the results of the Phoenix Lander.

	Scenario 1	Scenario 2	Scenario 3					Scenario 4
			I	II	III	IV	V	
pH	2	2-8	4	4	4	4	4	7.7
Mg ²⁺ (m)	0	4.97x10 ⁻⁴	4.97x10 ⁻⁴	4.97x10 ⁻³	4.97x10 ⁻³	4.97x10 ⁻³	4.97x10 ⁻⁴	7.34x10 ⁻⁵
Ca ²⁺ (m)	0	1.65x10 ⁻⁴	1.65x10 ⁻⁴	1.65x10 ⁻³	1.65x10 ⁻³	1.65x10 ⁻⁴	1.65x10 ⁻⁴	2.17x10 ⁻⁵
Na ⁺ (m)	0	2.50 x 10 ⁻⁵	2.50x10 ⁻⁴	2.50x10 ⁻⁴	2.50x10 ⁻⁵	2.50x10 ⁻⁴	2.50x10 ⁻⁴	charge balance
K ⁺ (m)	0	1.00 x 10 ⁻⁵	1.00x10 ⁻⁴	1.00x10 ⁻⁵	1.00x10 ⁻⁵	1.00x10 ⁻⁴	1.00x10 ⁻⁴	0.02968
Fe ²⁺ (m)	0	0	0	0	0	0	0	0
HCO ₃ ⁻ (m)	0	0	2.50x10 ⁻⁴	Atm CO ₂ *	Atm CO ₂ *	Atm CO ₂ *	Atm CO ₂ *	1.467
SO ₄ ²⁻ (m)	5x 10 ⁻³	5x 10 ⁻³ - 5x 10 ⁻⁹	1.65x10 ⁻⁴	1.00x10 ⁻⁵	2.50x10 ⁻⁵	2.50x10 ⁻⁴	1.00x10 ⁻⁴	0.587

* HCO₃⁻ was in equilibrium with atmospheric CO₂

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