Magnetite Authigenesis and the Warming of Early Mars

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Abstract: The Curiosity rover has documented lacustrine sediments at Gale Crater, but how liquid water became physically stable on the early Martian surface is a matter of significant debate. To constrain the composition of the early Martian atmosphere during sediment deposition, we experimentally investigated the nucleation and growth kinetics of authigenic Fe-minerals in Gale Crater mudstones. Experiments show that pH variations within anoxic basaltic waters trigger a series of mineral transformations that rapidly generate magnetite and H₂(aq). Magnetite continues to form through this mechanism despite high P CO₂ and supersaturation with respect to Fe-carbonate minerals. Reactive transport simulations that incorporate these experimental data show that groundwater infiltration into a lake equilibrated with a CO₂-rich atmosphere can trigger the production of both magnetite and H₂(aq) in the mudstones. H₂(aq), generated at concentrations that would readily exsolve from solution, is capable of increasing annual mean surface temperatures above freezing in CO₂-dominated atmospheres. We therefore suggest that magnetite authigenesis could have provided a short-term feedback for stabilizing liquid water, as well as a principal feedstock for biologically relevant chemical reactions, at the early Martian surface.

Keywords: Martian atmosphere, Mars Science Laboratory, redox, carbon dioxide, hydrogen

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In 2013, NASA’s Mars Science Laboratory Curiosity rover discovered an ancient fluvio-lacustrine environment in Gale Crater, Mars. Sedimentological, stratigraphic, and geochemical relationships document a freshwater lake that persisted at Gale crater for hundreds to thousands of years\textsuperscript{1,2}. Minerals, such as magnetite, and other compounds preserved in lacustrine mudstones, reflect redox-gradients and neutral to alkaline pH conditions within sediment pore waters during and soon after deposition\textsuperscript{3-7}. The paleo-environment captured by these deposits shares a distinct set of physical and chemical characteristics with some lake systems on the modern Earth, enabling detailed comparisons between the terrestrial and Martian sedimentary records of planetary habitability\textsuperscript{1,2}.

Nevertheless, the climate conditions that stabilized liquid water at Gale Crater are unknown. Although CO\textsubscript{2} is widely thought to have dominated the early Martian atmosphere\textsuperscript{8}, the Curiosity rover has only detected carbonate minerals at abundances significantly less than 1 wt. %\textsuperscript{3-6}. At the same time, climate models demonstrate that without additional gases, CO\textsubscript{2}-rich atmospheres could not have maintained surface temperatures above freezing\textsuperscript{9-10}. S-bearing volcanic species were previously thought to trigger greenhouse warming\textsuperscript{11-13}, but recent models show that S outgassing would have cooled the Martian surface rather than warming it\textsuperscript{14,15}. In the presence of elevated CO\textsubscript{2}, low abundances of H\textsubscript{2} and its reaction products (i.e., CH\textsubscript{4}) could have generated sufficient warming to stabilize liquid water\textsuperscript{16,17}, but plausible generation and delivery mechanisms for these species have remained elusive. For example, volcanic outgassing has been identified as a potential source of H\textsubscript{2}\textsuperscript{16}, but requires mantle redox states that would have limited CO\textsubscript{2} release\textsuperscript{18}. Although serpentinization has been implicated as a potential H\textsubscript{2} source on early Mars\textsuperscript{19}, orbital data indicate that serpentine is rare in Martian bedrock\textsuperscript{20}. In addition, because H\textsubscript{2}
production from terrestrial seafloor-hosted hydrothermal systems is controlled by a variety of kinetic factors\textsuperscript{21-22}, the H\textsubscript{2}-generating efficiency of Martian settings is poorly understood.

To constrain atmospheric composition at the time mudstones were deposited at Gale Crater, we experimentally simulated chemical processes that formed new, or authigenic, minerals soon after deposition. Comparing our experimental data with geological observations reveals that magnetite precipitation was likely triggered by the infiltration of groundwater into a lake equilibrated with a CO\textsubscript{2}-rich atmosphere. Experimental data also show that magnetite precipitation in Gale Crater mudstones would have been accompanied by the production of H\textsubscript{2}. Because H\textsubscript{2} and its reaction products can raise annual mean surface temperatures above freezing in CO\textsubscript{2}-dominated atmospheres\textsuperscript{17}, magnetite authigenesis could have provided a short-term feedback mechanism for stabilizing liquid water once climate conditions allowed it to infiltrate surface and subsurface reservoirs. We also show that geological observations by the Curiosity rover are consistent with both estimated timescales and predicted climatic shifts associated with transient H\textsubscript{2}-induced warming.

**Experimental evidence**

Reconstructing atmospheric composition from sedimentary rocks requires constraints on authigenic mineral formation pathways. The delivery of Fe\textsuperscript{2+}, Mg\textsuperscript{2+}, and SiO\textsubscript{2}(aq) to lake or sediment pore waters would have set the stage for mineral authigenesis as basaltic sediment was deposited, while increases in pH would have established the supersaturation necessary to precipitate authigenic minerals (Supplementary Text; Supplementary Figure 1). Under anoxic conditions (reflected, for example, by the preservation of detrital sulfides in some mudstones\textsuperscript{3}), Fe(II)-silicate, -oxide, or -carbonates all become supersaturated if pH increases in mudstone pore
waters (Supplementary Text; Supplementary Figure 1). However, a poor understanding of Fe(II)-mineral precipitation kinetics, including the origin of magnetite in Gale Crater mudstones, prohibits robust constraints on atmospheric composition\textsuperscript{23,24,25}.

We addressed these uncertainties with two experimental approaches. First, to investigate the nucleation and growth kinetics of authigenic Fe(II)-minerals in Gale Crater mudstones, we conducted precipitation experiments using synthetic Fe\textsuperscript{2+}, Mg\textsuperscript{2+}, and SiO\textsubscript{2}(aq)-bearing waters, modeled after those expected to form from reactions between water and basalt (Supplementary Text; Supplementary Figure 2). Experiments show that as these anoxic waters experience pH increases above \textasciitilde8.0, Fe\textsuperscript{2+} is withdrawn from solution, with minor decreases in Mg\textsuperscript{2+} and SiO\textsubscript{2}(aq) (Supplementary Figures 3 and 4). The loss of Fe\textsuperscript{2+} corresponds to a rapid decrease in the oxidation-reduction potential (ORP) of the system to values below the thermodynamic stability of H\textsubscript{2}O(l) at standard state conditions (Fig. 1A). This results from the production of reduced electro-active aqueous species during the initial stages of the experiments. The production of these species is transient, subsiding after several hours with a slow return to initial ORP values (Fig. 1A).

Solid phases extracted from the experiments show that increases in pH trigger the nucleation of Fe(OH)\textsubscript{2} (Fig. 1B). Once precipitated, ageing of Fe(OH)\textsubscript{2} at alkaline pH renders it unstable, even under strictly anoxic conditions; in minutes, Fe(OH)\textsubscript{2} rapidly transforms to green rust, a structurally related Fe(II)-Fe(III)-hydroxide (Supplementary Text; Supplementary Figure 5). As pH and strictly anoxic conditions are maintained, green rust transforms to magnetite in several days (Fig. 1B; Supplementary Text; Supplementary Figures 2 & 6).

Because the decomposition of Fe(OH)\textsubscript{2} is correlated with the production of reduced species during the first few hours of the experiments, the species must originate by accepting
electrons from Fe(OH)$_2$ as it transforms to green rust. The only aqueous species capable of forcing ORP below the thermodynamic stability limit of liquid H$_2$O is dissolved H$_2$ gas, which we have identified in our experiments at μmol/kg concentration (Supplementary Text). Once Fe(OH)$_2$ is transformed to green rust, H$_2$ production ceases and ORP recovers to pre-experiment values as H$_2$ exsolves to the reactor headspace (Fig. 1A).

To investigate the influence of dissolved CO$_2$ on authigenic Fe(II)-mineral pathways in Gale Crater mudstones, we conducted nucleation experiments in the Fe$^{2+}$-Mg$^{2+}$-SiO$_2$(aq) system as a function of pH and CO$_2$, again under strictly anoxic conditions. As above, when its solubility is exceeded, Fe(OH)$_2$ precipitates and transforms to green rust (Fig. 2). Fe(II)-carbonates also nucleate, but at supersaturations far above those predicted by equilibrium siderite solubility (Fig. 2). In fact, our experiments delineate an apparent critical supersaturation (K$_{crit}$) below which metastable solutions persist without Fe(II)-carbonate nucleation (Fig. 2). This value corresponds to the solubility of amorphous Fe(II)-carbonate (AFC) (Fig. 2). The formation of AFC, a highly transient solid, offers a low energy pathway to Fe(II)-carbonate formation. Upon ageing in solution, AFC may produce either siderite or chukanovite (Fe$^{II}_{2}$(CO$_3$)(OH)$_2$, metastable with respect to siderite$^{23,27}$, Supplementary Text; Supplementary Figure 7).

Finally, in experiments that are supersaturated with respect to both Fe(OH)$_2$ and AFC, mixtures of green rust-CO$_3$, siderite, and/or chukanovite are produced (Fig. 2). Under these conditions, the kinetics of Fe(OH)$_2$ precipitation and transformation to green rust are in competition with reactions leading to Fe(II)-carbonate (eventually producing siderite). These products are dominated by Fe(II)-carbonates relative to green rust, and green rust production becomes negligible as Fe(II)-carbonate supersaturation increases (Fig. 2).
**Groundwater infiltration into a CO\(_2\)-rich lake**

In contrast to recent thermodynamic models\(^{25}\), our experimental observations permit high atmospheric CO\(_2\) levels in equilibrium with the lake in Gale Crater. In the endmember case where CO\(_2\) represented the sole acid source to the lake, two processes would have controlled steady state lake water pH: (1) buffering by atmospheric P\(_{CO2}\) and, (2) alkalinity generated from the reaction between basaltic sediments and lake water. The relative importance of these two processes is a function of the ratio between total lake water mass and the mass of sediment reacting with the lake at any one time (water/rock ratio, or W/R). Although the precise water/rock ratio is poorly constrained, regional orbital and rover-based mapping indicate that the Gale Crater lake was aerially extensive and the water column was at least several meters deep\(^{1,2,5}\), suggesting that high mean water/rock ratios (i.e., >100) were likely the norm. Over the timescale of interest, kinetic calculations indicate that steady state lake water pH would have been poised between 5.2 and 5.6 at an atmospheric P\(_{CO2}\) of 1 bar and W/R ratios > 100, far below the nucleation threshold for Fe(II)-carbonate (K\(_{crit}\)) or Fe(OH)\(_2\) (Fig. 2; Supplementary Text; Supplementary Figure 8). Thus, under the conditions of our simulations, lake water pH is set by the input of CO\(_2\), formation of carbonic acid, and buffering by reaction with basaltic sediment. Calculations show that these pH conditions are sustained in the lake water body for thousands of years at all but the lowest water/rock ratios (i.e., where pH buffering by atmospheric CO\(_2\) can be overcome by water-rock interaction; Supplementary Text; Supplementary Figure 8).

Although maximum dissolved CO\(_2\) in the lake could have been high without precipitating Fe(II)-carbonate, geochemical and mineralogical data indicate that Fe(OH)\(_2\) solubility must have
been exceeded in sediments that preserve authigenic magnetite. This either requires that the entire lake body periodically experienced significant pH excursions to precipitate Fe(OH)$_2$ and eventually magnetite, or that local chemical perturbations to sedimentary pore waters drove magnetite precipitation. The topographic depression in which the Gale lake was situated resides at the lowest elevation for thousands of kilometers in any direction$^{2,28}$, and regional hydrological models predict that physical stabilization of a water body at this location involved a significant (up to 39-47% of the total influx) groundwater component$^{28}$. Our experimental constraints on magnetite and Fe(II)-carbonate precipitation kinetics permit a quantitative test of whether groundwater infiltration and mixing with lake water could have triggered magnetite precipitation, while inhibiting Fe(II)-carbonate formation.

To evaluate the role of groundwater infiltration on authigenesis in Gale Crater mudstones, constraints on subsurface aquifer chemistry are required. On Earth, groundwater percolating through basaltic aquifers is chemically distinct from surface waters$^{29-31}$. As meteoric water infiltrates mafic rocks, pH increases and atmospheric components are depleted along the flow path. These waters invariably become anoxic as O$_2$ reacts with Fe$^{2+}$, are devoid of dissolved CO$_2$ as carbonates precipitate$^{29-32}$, and commonly plateau at pH values of $\sim$10$^{31,32}$; Supplementary Text; Supplementary Figure 9).

With these constraints, we incorporated new experimental data for Fe(II)-mineral precipitation into a reactive transport model simulating groundwater infiltration into lacustrine sediments (Fig. 3, Supplementary Figures 10 and 11; Supplementary Text). Simulations of the diffusive transport and reaction between lake water and basaltic groundwater show that as groundwater infiltrated lacustrine sediments at Gale Crater, Fe(II)-carbonate saturation ($K_{\text{crit}}$) was never reached, and Fe(OH)$_2$ (eventually generating magnetite) precipitated instead (Fig. 3,
Supplementary Figures 10 and 11). This is because groundwater raises pore water pH upon mixing, but also dilutes dissolved CO\textsubscript{2} derived from lake water. Time resolved simulations show that magnetite authigenesis is sustained by the release of Fe\textsuperscript{2+} to pore waters from olivine present in the basaltic sediment delivered to the lake, which is the most reactive silicate present in Gale Crater sediments (Supplementary Text; Figure 3, Supplementary Figures 10 and 11). Under diffusion-dominated regimes, groundwater infiltration generates observed abundances of authigenic magnetite on thousand-year timescales (Supplementary Text). Thus our modeling results show that groundwater-lake water mixing is consistent with geochemical and mineralogical data from the Sheepbed member mudstones at the base of the stratigraphic section, and deep-water mudstones of the stratigraphically higher Murray formation, both of which contain abundant authigenic magnetite\textsuperscript{3,5,33,34}.

Alkaline groundwater would have also solubilized detrital silica minerals, explaining the magnetite-silica association observed specifically in deepwater mudstones of the Murray Formation\textsuperscript{5}. In fact, the dissolution and re-precipitation of silica polymorphs at high pH results in the formation of opal-CT in alkaline lake systems on Earth\textsuperscript{35}, providing a likely explanation for its presence in Murray mudstones.

Experimental and modeling data also show that groundwater infiltration and magnetite authigenesis at Gale Crater was accompanied by the production of H\textsubscript{2}(aq). Reactive transport simulations indicate that groundwater-lake water mixing produced H\textsubscript{2}(aq) at levels exceeding its solubility in ambient pressure aqueous solutions, therefore generating a free H\textsubscript{2} gas phase in the sediments (Figs. 1, 3). This result is consistent with abundant hollow nodules in Sheepbed member mudstones interpreted as voids formed by gas bubbles in the sediment during authigenesis\textsuperscript{1,36}. In fact, the size and abundance of these nodules agrees quantitatively with the
An authigenic H$_2$-CO$_2$ mechanism for warming early Mars

Low temperature H$_2$ production may have triggered a globally significant but transient feedback that warmed the early Martian surface and stabilized liquid water. Because a CO$_2$-rich atmosphere could not have stabilized liquid water by itself, adiabatic cooling would have transferred water ice to high altitude regions across much of the equatorial southern highlands$^{37,38}$. This implies that topographic lows would have received liquid water through episodic melting events. As melt water permeated surface and subsurface reservoirs in low-lying regions, pulses of magnetite authigenesis would have concentrated H$_2$ at their interface (Figure 3, Supplementary Figure 10). Therefore, the global authigenic H$_2$ flux would have been proportional to the total volume of sediments hosting groundwater-surface water mixing across the early Martian surface. Noachian to Hesperian open basin lakes represent at least ~1% of the present Martian surface$^{39,40}$, and this fraction is dominated by only a handful of lake basins located along the hemispheric dichotomy that are thought to have been groundwater-fed (on the basis of volume/catchment area)$^{39-41}$. However, the spatial distribution of these groundwater-fed lakes is also in agreement with hydrological models that predict a shallow groundwater table in Arabia Terra and the Eridania Basin$^{39,41-43}$, which together account for at least ten percent of the Martian surface. Thus, using minimum authigenic H$_2$ production rates for diffusion dominated regimes (from our reactive transport simulations) and applying a constant H$_2$ escape rate (valid for H$_2$-bearing atmospheres$^{17}$), we estimate that magnetite authigenesis alone could have led to percent-level atmospheric H$_2$ concentrations on early Mars if surface water-ground water mixing
was sustained, on average, over $10^4$ to $10^5$ years or less (Figure 4). In CO$_2$-dominated atmospheres, these H$_2$ concentrations would have promoted collision-induced absorption and sufficient warming to stabilize liquid water at the early Martian surface. This positive feedback would be significantly magnified if H$_2$ reacted to form CH$_4$\textsuperscript{16,17}. The duration of H$_2$-induced warming events would have been determined by H$_2$ escape and CH$_4$ photo-dissociation, restoring cold steady-state conditions through adiabatic cooling\textsuperscript{17}.

Geological data returned by the Curiosity rover are consistent with climatic shifts predicted by H$_2$-induced warming, as well as their characteristic timescales. The bulk composition of the Sheepbed member mudstone, at the base of the stratigraphic section examined by Curiosity, reflects low chemical index of alteration (CIA) values; these are consistent with sediment production under cold or arid climates\textsuperscript{1,4}. Shifts to progressively higher CIA values are recorded in the overlying Murray Formation, signaling climatic conditions that supported more effective chemical denudation\textsuperscript{5}. We predict that as H$_2$ gas was eventually lost from the Martian atmosphere, the lacustrine environment would have been driven to an increasingly water-limited state as liquid water stability became compromised.

Finally, H$_2$ produced in sedimentary systems on early Mars may have facilitated a wide range of biologically relevant chemical reactions. H$_2$ is an essential raw material in the synthesis of both atmospheric CH$_4$ and prebiotic organic compounds\textsuperscript{44,45}, and serves as a potent fuel for several autotrophic metabolisms\textsuperscript{46}. In fact, the acetyl-CoA pathway, one of the earliest bioenergetic metabolisms on Earth\textsuperscript{47,48}, is powered by the exergonic reaction between H$_2$ and CO$_2$ – components that both accumulated at the interface between lake bottom and groundwater on early Mars. Gale Crater stratigraphy, therefore, re-defines habitability of Martian surface
environments in specific chemical terms, and provides a crucial missing piece to the early Martian climate puzzle.

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calculations, and all authors analyzed the data. N.J.T. wrote the paper with contributions from J.A.H., I.A.M.A, and B.M.T.
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**Figure Captions:**

**Fig. 1.** Anoxic precipitation experiment with Mg$^{2+}$, Fe$^{2+}$, and SiO$_2(aq)$ bearing water. (A.) As pH is increased oxidation-reduction potential (ORP) falls below the thermodynamic stability of H$_2$O($l$), as H$_2(aq)$ is generated, which then slowly degasses to the reactor headspace. (B.) Under strictly anoxic conditions, pH increases precipitate Fe(OH)$_2$ which rapidly converts to green rust, in turn reducing H$_2$O($l$) and forming H$_2(aq)$. Metastable green rust transforms to magnetite in days. Error bars denote 2σ derived from triplicate experiments.

**Fig. 2.** Anoxic precipitation experiments as a function of pH and dissolved CO$_2$. Water compositions initially supersaturated with respect to Fe(OH)$_2$ (to the right of the blue dashed line) generate green rust through the transformation shown in Figure 1. Compositions initially supersaturated with respect to siderite (above the black line) do not generate Fe(II)-carbonate unless a critical supersaturation value (red line; $K_{crit}$) is crossed. Compositions supersaturated with respect to both Fe(II)-carbonate and Fe(OH)$_2$ yield mixtures of Fe(II)-carbonate and green rust; products are dominated by the former as supersaturation increases. 2σ derived from triplicate experiments is smaller than the symbols.
Fig. 3 Ground water-lake water mixing to form magnetite and $\text{H}_2(aq)$. (A.) Schematic of domain used in reactive transport simulations. (B.) Mineral volume fraction and $\text{H}_2(aq)$ concentrations in coexisting solutions plotted as a function of olivine reaction progress. Note that $\text{H}_2(aq)$ concentrations plotted here exceed the solubility of $\text{H}_2(aq)$ in ambient-pressure solutions, and would be expected to generate a free gas phase within the sediments. The curvature in $\text{H}_2(aq)$ is related to the diminishing reactivity of olivine as its volume fraction is depleted, and the increased diffusional gradient of $\text{H}_2(aq)$ out of the domain.

Fig. 4 Globally averaged authigenic $\text{H}_2$ production on early Mars. As surface and subsurface water reservoirs interact on early Mars and trigger authigenic magnetite precipitation, atmospheric $\text{H}_2$ concentration increases to percent levels over timescales of $10^4$ to $10^5$ years or less. Lines indicate atmospheric $\text{H}_2$ concentrations calculated at various percentages of the early Martian surface hosting authigenic $\text{H}_2$ production. Calculations apply a constant H-escape rate for $\text{H}_2$-bearing atmospheres\textsuperscript{17}. 
Methods:

Geological background of Gale Crater mudstones

Gale crater is situated in river-dissected terrain immediately south of the Martian dichotomy boundary. Gale crater formed at ~3.8-3.6 Ga, and the central portion of the crater contains sedimentary deposits that form a large mound (Mt. Sharp) that is cored by a central peak. After formation, Gale Crater was infilled with alluvial fan and lacustrine sediments that were deposited and exhumed before 3.3-3.1 Ga. The sedimentology and stratigraphy of Gale crater sedimentary rocks are described extensively in Grotzinger et al.; a brief summary of salient relationships is provided here. At the base of the stratigraphic section investigated by the Curiosity rover lies a thick sequence (>75 m) of mostly fluvial-deltaic sandstones and conglomerates known as the Bradbury group. The Bradbury Group contains a basal unit, called the Yellowknife Bay formation, which is composed in part of lacustrine mudstones. These mudstones are named the Sheepbed member of the Yellowknife Bay formation. To the south of Curiosity’s landing site, the Bradbury group interfingers with, and is ultimately overlain by, a thick sequence (>100m) of lacustrine mudstones, called the Murray formation. Both the Bradbury group and Murray fm. were buried to substantial depth (hundreds to thousands of meters), and then exhumed by eolian erosion. Mudstone deposits of the Sheepbed member and the Murray fm. are predominantly composed of fine-grained rock (< 64 micron grain size) displaying massive (in the case of the Sheepbed member) to laminated (mm to cm-scale) bedding (in the case of the Murray formation), characteristic of deposition under quiescent conditions in a lake.
All mudstones examined by the Curiosity rover through ~sol 1300 contain magnetite of probable authigenic origin, in abundances ranging from 3.0-8.0 wt. %\(^3,5,33,34\). Potential controls on the bulk chemical composition and relative abundances of minerals and mineraloids in the mudstones of Gale Crater have been described extensively\(^3,5,33,34,55\). A brief summary based is provided here. The mudstone strata at Gale crater record the following sequence of events: (i) at the base of the section, in the Sheepbed member, mudstones were deposited under cold climate conditions, as evidenced by low values of the Chemical Index of Alteration (ranging from 30-37%). Sheepbed member sedimentary rocks contain detrital sulfide minerals (pyrhotite and pyrite), magnetite of probable authigenic origin, and Mg-Fe-rich smectite, all consistent with formation under anoxic conditions at neutral to alkaline pH. (ii) The stratigraphically higher Murray formation was deposited under comparatively warmer and wetter climate conditions, as evidenced by increased CIA values (ranging from 30-53%) relative to those exhibited by the Sheepbed member. The mineralogy and geochemistry of the Murray formation are consistent with deposition in a neutral-alkaline pH, redox-stratified lake environment, in which oxidized Fe-minerals (especially hematite) and phyllosilicates dominated the shallow, more oxidizing portion of the lake, while authigenic magnetite and silica were formed in anoxic waters in deeper portions of the lake.

**Kinetic model of mineral dissolution**

In order to investigate the influence of sediment composition on fluid chemistry in Gale Crater mudstone pore waters, we constructed a kinetic model of mineral dissolution examining the interaction of dilute water with crystalline basalt of identical composition to Rocknest, a basaltic soil deposit that was analyzed by the Curiosity rover in Gale Crater using X-ray fluorescence and X-ray diffraction techniques\(^56,57\). Rocknest represents an ideal starting material for our
simulations because it is a recent eolian soil with a basaltic bulk composition similar to that of average Martian crust and the Sheepbed mudstones, which has experienced little chemical modification due to water-rock interaction\cite{Blake2015}. Amorphous material reported by Blake et al.\cite{Blake2015} was not included in the model; instead, we focus on the crystalline mineralogy, which comprises 67 wt.% of the Rocknest deposit. The amorphous component is likely composed of a mixture of volcanic glass and poorly crystalline to amorphous mineraloids formed by alteration of that glass\cite{Blake2015}, neither of which can be reliably incorporated into a thermodynamic model of water-rock interaction. In our model, a total mass of crystalline minerals equal to 67 g was multiplied by factors ranging from 0.01-100 to adjust water/rock ratios in the presence of a constant 1 kg water. The model was run with Geochemists Workbench version 11\cite{Blair2015} software, and thermodynamic data from the LLNL database\cite{Wong2015}. Mineral dissolution rates are treated according to the general equation:

$$ r = A_S k a_{H^+}^n \left(1 - \frac{Q}{K}\right) $$

where $r$ is the rate of dissolution, $A_S$ is the specific surface area, $k$ is the rate constant, $a_{H^+}$ is the dependence of the dissolution reaction on the proton concentration raised to the exponent $n$, and $Q$ and $K$ are the activity product and equilibrium constant for the dissolution reaction, respectively.

Parameters for calculating mineral dissolution rates are listed in Table S1. End member crystalline minerals were added as reactants in corresponding proportions to mineral chemistry and relative abundances for the Rocknest target reported in Blake et al.\cite{Blake2015}. Surface areas were held constant at 1000 cm$^2$ g$^{-1}$, based on an average particle size of <50 microns for mudstones in
Gale Crater (from MAHLI images; 1)) and general particle size-surface area relationships for silicate minerals reported by Brantley et al.60. Rate constants for mixed composition silicates were calculated as weighted averages of log rate constants of the end members (as described in Brantley & Conrad61, and then these were applied to all end members from which the rate constant was derived. In this way, realistic dissolution behavior of mixed composition silicates can be determined. Exponential pH dependencies ($a_{H^+}$) were taken from Bandstra & Brantley62. Typical model results are depicted in Figure S1.

The results of the model show that olivine dissolution strongly affects the chemistry of initially dilute waters by releasing Mg$^{2+}$, SiO$_2$(aq) and Fe$^{2+}$ into solution more rapidly than other rock-forming silicates (Figures S1A and S1B). Thus, the initial chemistry of sediment pore waters will reflect this interaction. Progression of this aqueous system to alkaline pH results in supersaturation with several possible minerals, some of which are depicted in Figure S1C. This general chemical system was used as a starting point in experiments, discussed below, which examined mineral precipitation in Fe$^{2+}$, Mg$^{2+}$ and SiO$_2$-containing systems as a function of pH and $P_{CO_2}$. Finally, the kinetic model results predict fluid chemistries (i.e., Figure S1A) that are in quantitative agreement with water-rock interaction experiments conducted on synthetic Martian basalt of nearly identical mineralogical composition (reported in Tosca et al.63).

Experimental methods

Precipitation experiments were conducted to examine the competitive nucleation and growth of authigenic mineral phases that may become supersaturated in basalt-dominated sedimentary systems on Mars. Starting compositions of solutions were chosen based on results of the kinetic model described in the previous section, an example of which is indicated in Figure S1. The
interaction between fine-grained basaltic sediment and surface waters on early Mars is controlled by: the starting lithology of the basaltic material, the effective water-to-rock ratio, the initial pH, reactive surface area of sediment, and composition of the initial fluid. As discussed in the previous section, of these variables only the starting lithology of basaltic material, and, to some degree, the particle size and thus surface area, are constrained. Thus, our water-rock interaction model explores variable water-to-rock ratio (between 1 and 1000, by weight), variable initial pH (between 1 and 4) conditions. These parameters overlap with water-to-rock ratios and initial pH of experimental basalt dissolution experiments conducted by Tosca et al. (2004), and, as discussed in the text, cation concentrations are in quantitative agreement with that study, which examined fine-grained olivine-bearing basaltic material (i.e., compare Figure S1A concentrations with Figure A3E in Tosca et al., 2004). We observe that at fixed surface area and lithology, cation concentrations are controlled mainly by initial pH. In addition, the relative concentrations of the most abundant solutes (i.e., Mg$^{2+}$, Fe$^{2+}$ and SiO$_2(aq)$ are essentially fixed by the presence of olivine, the most reactive rock-forming mineral in the sediment (similar to conclusions based on experiments by Tosca et al. 2004). Thus, the starting fluid compositions for experiments conducted in this study examined high, low and average total solute concentration arising from model runs (corresponding to low, high and average initial pH values examined in the model). These are: Mg$^{2+}$: 0.1-20 mmol/kg, Fe$^{2+}$: 0.04-16 mmol/kg, and SiO$_2(aq)$: 0.08-18 mmol/kg. Because initial nucleation experiments showed that that the concentrations of Mg$^{2+}$ and SiO$_2(aq)$ relative to Fe$^{2+}$ exerts a negligible control on the rates and mechanisms of precipitation and transformation of Fe-bearing minerals in this system, we set these three components equal to each other for the remaining experiments we pursued, some of which are reported herein.
We employed a simple chemical reactor that allowed the tracking of Fe$^{2+}$, Mg$^{2+}$, and SiO$_2$(aq) in synthetic solutions at various fixed pH levels (Figure S2). Experiments were conducted in 1L borosilicate glass reaction vessels triple-wrapped in Al-foil (to prevent UV photolysis from fluorescent lights$^{64}$ and continuously stirred. Anoxic nucleation experiments were conducted in triplicate to assess repeatability. To maintain strictly anoxic conditions during experimentation, the vessel was housed in a Coy polymer anaerobic chamber. The anaerobic chamber was purged with a 4% H$_2$ / 96% N$_2$ gas mixture, maintaining an anoxic atmosphere through the use of a Pd catalyst and desiccant connected to a re-circulating fan box. The Pd catalyst scrubs O$_2$ from the system by continuously reacting trace O$_2$ with available H$_2$ in the chamber, and the resulting H$_2$O is then adsorbed onto a desiccant. The gas composition of the anaerobic chamber was continuously monitored with a Coy gas analyzer and the atmosphere was maintained at <1ppm O$_2$(g) throughout the duration of all experiments and any associated sample preparation or analysis. To facilitate analysis of H$_2$(aq) produced during the experiments, a subset of experiments was repeated after the anaerobic atmosphere was purged and replaced with ultra-pure argon. The anaerobic chamber was maintained in this condition for several days to allow purging of remnant N$_2$/H$_2$ gas mix and several process blanks were taken on de-ionized water as a comparison to solutions for which H$_2$ was analyzed (described below).

All aqueous solutions introduced into the anaerobic chamber were first purged of dissolved O$_2$ by bubbling O$_2$-free N$_2$ gas through the solution for at least 45 minutes before transfer to the glovebox$^{65}$. Solutions were then left in the glovebox and repeatedly shaken and mixed for a further 2-3 days to allow any remaining O$_2$ to escape. Before experiments were started, the absence of dissolved O$_2$ was verified using the indigo carmine blue method$^{66}$. Synthetic solutions were generated by the addition of relevant components (i.e., Mg, Fe, SO$_4$ and Cl). SiO$_2$(aq) was
added by the addition of tetraethoxysilane (TEOS), which was allowed to equilibrate in the solution for ~48 hours. Fe^{2+} was added using stock solutions that were freshly prepared prior to each experiment from de-oxygenated de-ionized water and Mohr’s salt \((\text{NH}_4)_2\text{Fe}^{2+}(\text{SO}_4)_2\cdot6\text{H}_2\text{O})\). Mohr’s salt is highly resistant to oxidation and was shipped from the supplier under N\(_2\) gas and opened in the anaerobic chamber upon delivery.

In all experiments, pH was maintained at constant levels (between 7.0 and 9.0) using a Metrohm titrino 848 auto-titrator installed in the anaerobic chamber (Figure S2). Titration in these experiments was accomplished with 0.1 mmolal NaOH via a suspended tube to prevent precipitation at the titrant source. Rates of NaOH addition varied between a maximum of 10 mL/minute and a minimum of 10 \(\mu\)L/min. Some experiments also achieved constant pH through the use of the MOPS (3-(N-morpholino) propanesulfonic acid) buffer which exhibits negligible metal complexation in solution due to steric hindrance of functional groups\(^67\).

Experiments were initiated upon titration to the desired pH level from a starting point of approximately 4. pH and oxidation reduction potential (ORP) were continuously monitored throughout the experiments. ORP was measured with a Pt electrode and was calibrated against freshly prepared ZoBell’s solution\(^68\). This was used to periodically establish the temperature dependence of the Ag/AgCl reference electrode, and correct measured values. ORP readings were taken once values were stable to within 5 mV. Standard deviations of these readings were derived from experiments repeated in triplicate. Solution samples were withdrawn periodically and filtered through 0.1 \(\mu\)m nylon syringe filters in the anaerobic chamber and immediately acidified with 4% HNO\(_3\) for subsequent elemental analysis. Solids were extracted periodically from the reactor, treated with a mini-centrifuge in the anaerobic chamber, decanted, and immediately mounted on a silicon substrate in the anaerobic chamber for powder diffraction.
analysis (described below). Upon experiment termination, the solution was vacuum filtered through a 0.1 μm nylon filter membrane in the anaerobic chamber. The filter and precipitate were wrapped in Al foil and allowed to dry under the low-humidity anoxic atmosphere before aliquots were taken for solid-phase analysis.

Experiments evaluating CO₂ dependence on mineral precipitation were repeated using closed borosilicate vessels with zero headspace to prevent CO₂ degassing from solution. CO₂ was added as NaHCO₃ which was allowed to equilibrate in solution at a given pH set by the MOPS (3-(N-morpholino) propanesulfonic acid) buffer. Experiments were started via the delivery of Fe²⁺ from stock solution by passing a syringe through a sealed septum, and were continuously shaken with an orbital shaker throughout the duration of the experiment. As above, all experiments were triple wrapped in Al foil and conducted in the anaerobic chamber.

**Analytical methods**

Solution analyses of major cations (Mg, Fe₂⁺, Si) were performed via solution-phase inductively coupled plasma mass spectrometry (ICP-MS). All solutions were diluted in ultra-clean 4% HNO₃ and utilized matrix-matched element standards chosen at levels to bracket analyte concentrations.

As a consistency check and for real-time monitoring, periodic analyses of dissolved ferrous iron, total iron, SiO₂(aq) and SO₄ or Cl were performed using a HACH DR2800 bench top UV/vis spectrophotometer and the 1,10-phenanthroline, heteropoly blue and barium sulfate methods, respectively.

Once extracted in the anaerobic chamber, solid material precipitated during the experiments was analyzed by powder X-ray diffraction (XRD) using a Panalytical Empyrean diffractometer.
utilizing a Co Kα source, operated at 40 kV and 40 mA, and scanned between 5-65 degrees 2Θ. Powders were prepared as smears on zero background single crystal silicon substrates after centrifugation and decanting. Samples were prepared and mounted sample holders in the anaerobic chamber, and sealed with kapton foil prior to analysis, and/or treated with glycerol, both of which effectively prevented any oxidation during preparation and analysis well beyond the data collection period (less than 15 minutes).

Rietveld refinements were performed on experimental powder patterns using the GSAS-II software package\textsuperscript{69}. Instrument parameters were determined by refining powder patterns collected under identical experimental conditions for polycrystalline Si (sample NIST 640c). Structural models for refinements of magnetite and Fe(OH)\textsubscript{2} were taken from Fleet\textsuperscript{70} and Parise et al.\textsuperscript{71}, respectively.

H\textsubscript{2} analysis was conducted on a series of solution samples taken from one interval of a duplicate experiment to confirm H\textsubscript{2} production as indicated by electrochemistry measurements. Samples were extracted using gas-tight syringes and analyzed on a Agilent micro GC/MS equipped with a TCD/FID detector system and Ar carrier gas. Process blanks (de-ionized water collected from the reaction vessel) were run in triplicate to establish a baseline before experimental samples were run, also in triplicate. The averaged H\textsubscript{2}(aq) concentration measured in the process blanks was 33 ± 8 \times 10^{-9} \text{ mol/kg}.

Code availability

Two computer codes were used to generate results discussed in this manuscript: (1) Geochemist’s Workbench (v11) and (2) PFLOTRAN (http://www.pflotran.org). Geochemist’s
Workbench is a proprietary code under copyright, maintained, and sold through Aqueous Solutions LLC; availability is not associated with this manuscript. PFLOTRAN is an open-source code available through http://www.pflotran.org. This code, utilizing thermodynamic and kinetic quantities described herein, can be used to generate results presented in this manuscript.

Data availability

The datasets generated and/or analysed during the current study are available from the corresponding author on reasonable request.
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A. Start of experiment

- Thermodynamic $H_2O(l)$ - $H_2(g)$ boundary
- $H_2(aq)$ exsolution to headspace
- $H_2(aq)$ production

B. $pH = 8.7$

- 3 days: 1000, 001 Fe(OH)$_2$
- 20 min: 003 Fe(OH)$_2$
- 2 min: 003 Fe(OH)$_2$
- 1 min: 003 Fe(OH)$_2$
Co2(g) (fugacity)

pH

25°C

Siderite

Fe-carbonate (siderite and/or chukanovite)

Green rust (Cl or CO3)

Fe(II)-carbonate ($K_{crit}$)

- To pH 6.7 at $f_{CO2} = 1$
- To pH 5.3 at $f_{CO2} = 1$
Diffusive lake water flux

Diffusive groundwater flux

Sediment-water interface

Olivine-bearing sediment (porosity = 0.6)

A.

Mineral Volume Fraction

Olivine reacted

$H_2(aq)$ (molal)

0.10

0.08

0.06

0.04

0.02

0.00

0.0 0.2 0.4 0.6 0.8 1.0

0.25

0.20

0.15

0.10

0.05

0.00

0.00

0.02

0.04

0.06

0.08

0.10

0.15

0.20

0.25

B.

Olivine

Magnetite

$H_2(aq)$ (molal)

Olivine reacted

0.0

0.2

0.4

0.6

0.8

1.0
