



Geochemistry constrains global hydrology on Early Mars

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ABSTRACT

Ancient hydrology is recorded by sedimentary rocks on Mars. The most voluminous sedimentary rocks that formed during Mars' Hesperian period are sulfate-rich rocks, explored by the *Opportunity* rover from 2004–2012 and soon to be investigated by the *Curiosity* rover at Gale crater. A leading hypothesis for the origin of these sulfates is that the cations were derived from evaporation of deep-sourced groundwater, as part of a global circulation of groundwater. Global groundwater circulation would imply sustained warm Earthlike conditions on Early Mars. Global circulation of groundwater including infiltration of water initially in equilibrium with Mars' CO₂ atmosphere implies subsurface formation of carbonate. We find that the CO₂ sequestration implied by the global groundwater hypothesis for the origin of sulfate-rich rocks on Mars is 30–5000 bars if the *Opportunity* data are representative of Hesperian sulfate-rich rocks, which is so large that (even accounting for volcanic outgassing) it would bury the atmosphere. This disfavors the hypothesis that the cations for Mars' Hesperian sulfates were derived from upwelling of deep-sourced groundwater. If, instead, Hesperian sulfate-rich rocks are approximated as pure Mg-sulfate (no Fe), then the CO₂ sequestration is 0.3–400 bars. The low end of this range is consistent with the hypothesis that the cations for Mars' Hesperian sulfates were derived from upwelling of deep-sourced groundwater. In both cases, carbon sequestration by global groundwater circulation actively works to terminate surface habitability, rather than being a passive marker of warm Earthlike conditions. *Curiosity* will soon be in a position to discriminate between these two hypotheses. Our work links Mars sulfate cation composition, carbon isotopes, and climate change.

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1. Introduction

Liquid water flowed over the surface of Mars billions of years ago, and aqueous minerals also formed kilometers below the surface (e.g., McLennan and Grotzinger, 2008; Ehlmann et al., 2011). However, the extent of hydrologic coupling between the surface/near-surface and deep subsurface on Early Mars is unknown. In one view, continuous permafrost isolated the deep hydrosphere from the surface, with only local and transient exceptions (e.g., Fastook and Head, 2015; Fairén, 2010; Schwenzer et al., 2012). In another hypothesis, surface and deep-subsurface waters repeatedly swapped places as part of a prolonged global groundwater cycle – vertical integration enabled by $>10^{7-8}$ yr of annual-averaged surface temperatures above the freezing point (Andrews-Hanna et al., 2010). The existence and extent of global deep-groundwater cycling are key unknowns for Early Mars climate and global hydrology (Wordsworth, 2016), water loss (Usui et al., 2015), and habitability (Onstott et al., 2019). Moreover,

global deep-groundwater flow could piston atmospheric CO₂ into the deep subsurface and fix it as deep carbonates. Uncertainty in the size of the deep carbonate reservoir is a major uncertainty in Mars' CO₂ evolution (e.g. Jakosky and Edwards, 2018; Jakosky, 2019).

Central to the question of vertical isolation versus vertical integration of Early Mars' hydrosphere is the archive of ancient hydrology contained within mostly Hesperian-aged (3.6–3.2 Ga, based on crater chronology) sulfate-bearing sedimentary rocks (Malin and Edgett, 2000; Bibring et al., 2007). This rock type was ground-truthed by the Mars Exploration Rover *Opportunity* investigation of the Burns Formation at Meridiani (e.g. Squyres et al., 2006). At Meridiani, texture and mineralogy record multiple stages of diagenesis – involving acid and oxidizing near-surface groundwater (Fig. 1) (McLennan and Grotzinger, 2008). Burns Formation sandstones are ~40 wt% {Mg,Fe,Ca}SO₄. The cations for the sulfates were initially interpreted to be derived from slow wicking-to-the-surface and evaporation of deep-sourced saline groundwater, as part of a global groundwater circulation that could also explain the low elevations of the sulfate-bearing rocks (Andrews-Hanna et al., 2010). The rocks must have been altered in pH = 2–4 waters in order to explain the detection of jarosite (Tosca et al., 2008).

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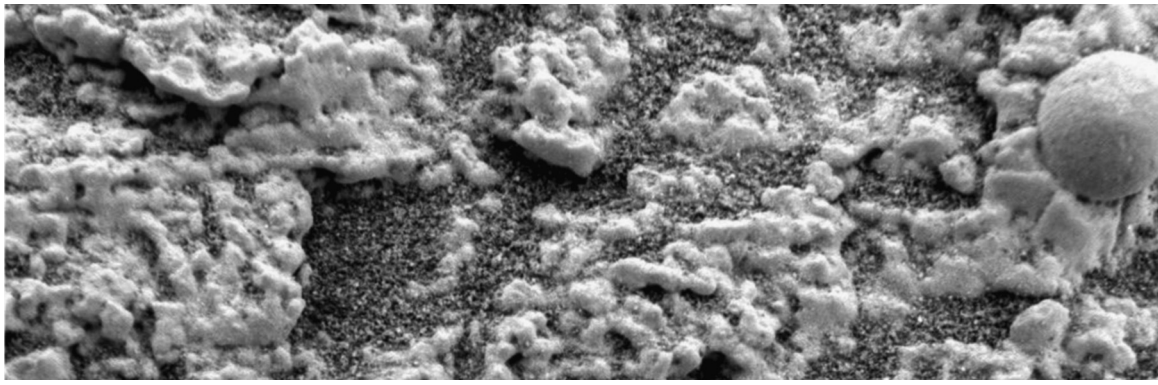


Fig. 1. Evidence for shallow-diagenetic alteration of the Burns Formation, Meridiani, Mars. Image is ~ 3 cm across. Laminae separated by <1 mm have different degrees of cementation. Halo girdles Fe_2O_3 concretion at right. Subframe of 1M130671710EFF0454P2953M2M1, Opportunity rover Microscopic Imager, sol 28. (After Grotzinger et al., 2005).

The jarosite presumably formed near the surface. There, $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation (by UV photons, or by atmospheric O_2), or volcanic H_2SO_4 , could drive acidity (Tosca et al., 2008; Baldrige et al., 2009; Hurowitz et al., 2010; Nie et al., 2017). Opportunity's mapping of sulfate-bearing sedimentary rocks that experienced acid and oxidizing alteration (driving the formation of jarosite and hematite) has been extended by orbital surveys. Sulfate-bearing sediments ($>10^6$ km³ in total) extend across much of Meridiani (5°S – 10°N); Valles Marineris and nearby chaos (0 – 15°S); and Gale crater (5°S), among other sites (Bibring et al., 2007; Hynek and Phillips, 2008; Grotzinger and Milliken, 2012). Stratigraphic thicknesses of >2 km suggest millions of years of deposition. Thus, if groundwater circulation was the engine of sulfate formation, then the sulfate-bearing sedimentary rocks are evidence for millions of years of warm Earthlike conditions on Early Mars.

However, the Hesperian global deep-groundwater circulation hypothesis is disputed. For example, the sulfates themselves have been proposed to form at 220–270 K by acid-rock reactions (Niles and Michalski, 2009; Niles et al., 2017). The textural evidence for shallow flow of groundwater (Fig. 1) might be explained by a shallow, local source of water, such as seasonal meltwater (Kite et al., 2013a). The survival (within sedimentary rocks) of fragile minerals that would have been dissolved by high water/rock ratio alteration at depth argues against persistent circulation (e.g. Dehouck et al., 2017; Phillips-Lander et al., 2019). The low variation of K/Th (5300 ± 220) on Mars' surface at 300 km scales is an independent argument against global groundwater circulation (Taylor et al., 2006). Potassium is much more mobile than thorium, and so extensive aqueous alteration of the crust would be expected to enhance K at evaporation zones. But this is not observed (Taylor et al., 2006). Therefore, the existence or otherwise of a global and deep groundwater circuit on Early Mars remains an open question. Nevertheless, there is abundant evidence for groundwater movement on Early Mars: mineralized fracture-fills including Ca-sulfate veins are widespread (e.g., Okubo and McEwen, 2007; Yen et al., 2017). Moreover, de-watering drove sediment deformation during early diagenesis at some sites (Rubin et al., 2017), and water was released from the subsurface to form some chaos terrains and associated outflow channels (Carr, 2006). However, the duration and cause of all these flows remains unclear. In summary, the sulfate-bearing sedimentary rocks were altered by shallow groundwater (McLennan et al., 2005), but there is no consensus as to whether or not Hesperian Mars had a global hydrologic cycle including deep groundwater.

2. Global groundwater circulation implies carbonate sequestration if recharge waters equilibrated with the atmosphere

Here, we test the global deep-groundwater hypothesis for formation of the Hesperian sulfates. We do this by tracing the hypothesis' implications for carbon sequestration and thus global atmospheric and climate evolution (Fig. 2). Our starting point is that CO_2 -charged water is out-of-equilibrium with the basaltic crust of Mars. As a result, initially atmospherically-equilibrated water percolating along the long flow paths entailed by the global deep-groundwater hypothesis ($>10^3$ km; Andrews-Hanna et al., 2010) should deposit C as carbonate (e.g. Griffith and Shock, 1995; Niles et al., 2013; Tomkinson et al., 2013; Melwani Daswani et al., 2016). Carbonate formation is inevitable for very long and deep flow paths through basalt, and mechanisms that could inhibit carbonate formation in the surface/near-surface (e.g. Bullock and Moore, 2007) do not apply here. (Even for relatively short and shallow groundwater flow-paths, carbonate precipitation from groundwater has occurred on Mars: e.g. van Berk et al., 2012; Ruff et al., 2014.) Once emplaced deep within basalt, Hesperian carbonates should persist. That is because (unlike Earth) post-3.6 Ga Mars lacked a mechanism to heat carbonates to drive off CO_2 , such as plate tectonics or global volcanism (Ogawa and Manga, 2007), except locally (Glotch and Rogers, 2013). Therefore, deep groundwater circulation between the atmosphere/surface and the basaltic crust of Mars implies one-way geologic sequestration of CO_2 (Niles et al., 2013) (Fig. 2).

By estimating the magnitude (C_{seq}) of the implied Hesperian CO_2 sequestration, we can test the global groundwater hypothesis. Possible outcomes of our test are:

- $C_{\text{seq}} > 10$ bar: If C_{seq} exceeds Mars' total estimated outgassed CO_2 inventory (1–10 bar; Stanley et al., 2011; Lammer et al., 2013), then the deep-global groundwater hypothesis and our understanding of Mars' composition are not consistent with one another.
- $C_{\text{seq}} > 1$ bar: If C_{seq} exceeds the CO_2 in the atmosphere at 3.6 Ga plus the amount of CO_2 outgassed 3.6–3.2 Ga (a subset of Mars' total estimated CO_2 inventory, because of pre-3.6 Ga CO_2 loss; Kite et al., 2014), then the deep-global groundwater hypothesis predicts a very thin atmosphere. In that case, the deep-global groundwater hypothesis is not consistent with the widely-held belief (Haberle et al., 2017) that an atmospheric pressure >0.1 bar is needed for extensive liquid water at the surface of Early Mars.
- $C_{\text{seq}} < 1$ bar: If C_{seq} is <1 bar, then there is no tension between the deep-global groundwater hypothesis and our under-

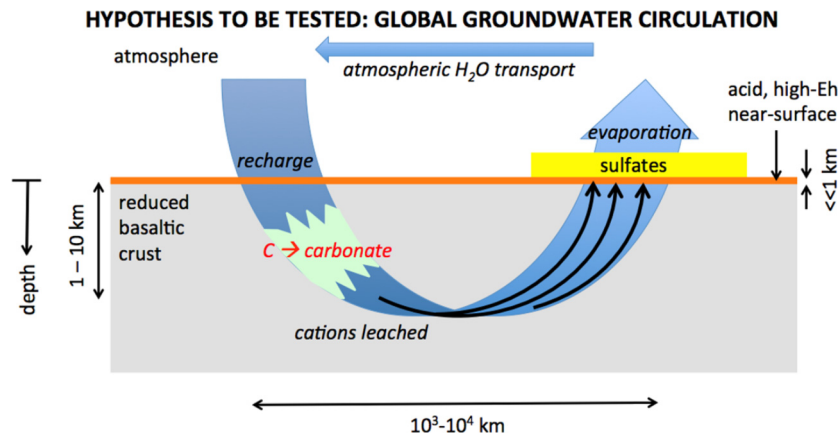


Fig. 2. The prevailing view of sulfate origin, to be tested here. Formation of sulfates from deep-sourced cations implies C sequestration by carbonate formation.

standing of Mars history. However, $C_{seq} > 0.1$ bar would imply atmospheric drawdown and thus climate change during the time of deposition of the sulfate-rich sedimentary rocks (if the deep-global groundwater hypothesis is correct).

3. Method

Unfortunately, C_{seq} is poorly constrained by existing observations. Although crustal carbonates are observed in Mars meteorites (Bridges et al., 2001), and from Mars orbit (Wray et al., 2016), the quantity of crustal C on Mars is very uncertain. (The source of C for the crustal carbonates is often also uncertain – C degassed from intrusions, as well as C leached from crystalline rocks, are alternatives to drawdown of atmospheric C.) Carbonate is not detected at most locations on Mars. If (on this basis) we were to assign an upper limit of 1 wt% carbonate to Mars' topmost 10 km of crust, then the corresponding upper limit on sequestration would be ~ 4 bars. 4 bars exceeds Mars' total estimated outgassed CO_2 inventory (Lammer et al., 2013). Therefore, currently published data provide little guidance on the partitioning and fate of Mars C.

Therefore, we use a fluid-centered flow-through geochemical model (CHIM-XPT; Reed, 1998), combined with global mass balance, to test the deep-groundwater hypothesis by finding C_{seq} . This test requires answers to two sub-questions:

- (1) **How much water is needed to make the Hesperian sulfate-bearing rocks (§4.1)?**
- (2) **How much C is sequestered per unit water?** (How much of the initial C dissolved into water at the recharge zone goes into carbonate, and how much survives to reach the upwelling zone?) (§4.2).

For our CHIM-XPT calculations, our basalt (aquifer-host) rock composition is based on Mars rover measurements of fresh Mars basalt (McSween et al., 2006) and is as follows: 46.22 wt% SiO_2 ; 10.88 wt% Al_2O_3 ; 2.14 wt% Fe_2O_3 ; 17.08 wt% FeO; 0.44 wt% MnO; 10.49 wt% MgO; 8.35 wt% CaO; 2.66 wt% Na_2O ; 0.11 wt% K_2O ; 0.64 wt% P_2O_5 ; 0.84 wt% FeS; and 0.15 wt% Cl. To take account of the possibility of incongruent basalt dissolution (Milliken et al., 2009), we also considered a pure-olivine composition. Our olivine composition is also based on Mars-rover measurements for little-altered basalt (McSween et al., 2006) and is as follows: 34.75 wt% SiO_2 ; 42.39 wt% FeO; 22.86 wt% MgO (zero CaO).² Precipitation of many minerals is suppressed for kinetic reasons. We do not explicitly

consider Mars upper crust permeability in our model. The mean value of permeability is currently unknown, and estimated to lie in the range (10^{-11} – 10^{-15}) m^2 (by Hanna and Phillips, 2005) for Mars' upper crust. For Mars' upper crust, permeability likely varies by orders of magnitude regionally (Harrison and Grimm, 2009), and likely also varied with time on Hesperian Mars due to the competition between fracture-sealing processes (such as carbonate mineral precipitation within fractures), and fracture creation (by tectonics, impacts, and cracking to accommodate magmatic intrusions) (Sleep and Zoback, 2007). In effect we assume permeability is high enough that permeability is not limiting for deep, global groundwater circulation. Thus, our upper bounds on the vigor of deep global groundwater circulation only become stronger if we are wrong about permeability. Our runs assume an atmosphere with minor O_2 (as for present Mars), but running with zero O_2 would not affect the conclusions. That is because any dissolved oxygen is quickly consumed at $W/R > 10^4$ by early $\text{Fe}(\text{OH})$ precipitation, and the fluid subsequently stays fairly reduced along the flow path. Runs are carried out at 0.01 °C, which is thought to be appropriate for the near-surface of Early Mars. Details on our CHIM-XPT runs are contained in the Supplementary Information.

4. Results

4.1. How much water is needed?

We use two methods to estimate the water demand if global-groundwater circulation was the engine of Hesperian sulfate formation. One method is based on jarosite stability (Hurowitz et al., 2010), and the other method is based on cation supply. The larger of the two is the relevant constraint for the hypothesis that deep-sourced groundwater supplied the cations for the sulfates at Meridiani. This turns out to be the cation supply constraint.

Both methods require rock volume as input. The volume of sulfate-bearing sedimentary rock on Mars is $> 3.4 \times 10^5 \text{ km}^3$ today (Michalski and Niles, 2012; Hynek and Phillips, 2008). The outcrops have eroded surfaces, so were once more voluminous. Moreover, the layers in the sulfates were originally very close to flat in the deep-groundwater hypothesis, in contrast to the $\sim 10^\circ$ topographic slopes and $\sim 5^\circ$ layer dips measured for outcrops today (Kite et al., 2016). Thus, in the deep-groundwater hypothesis, erosion has removed (87–92)% of the original volume of sulfate-bearing sedimentary rocks, which is implied to be 2.9 – $4.0 \times 10^6 \text{ km}^3$ (Andrews-Hanna et al., 2010; Andrews-Hanna, 2012; Michalski and Niles, 2012; Zabusky et al., 2012). (This entails a very large pre-erosion S content. It is unclear where this S could have been sourced from, and where it could be hidden today; Michalski and Niles, 2012.)

² In-situ X-ray diffraction data for residual Ol in Gale sediments is more Mg-rich (Morrison et al., 2018), as expected for water-altered sediments (Stopar et al., 2006).

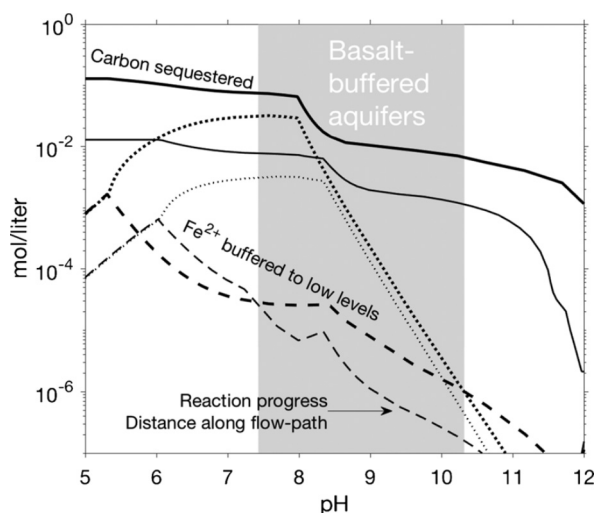


Fig. 3. CHIM-XPT output for water-basalt interaction for 0.2 bars (thin lines) and 2 bars $p\text{CO}_2$ (thick lines). Solid lines show total C in aqueous fluid, which decreases as carbon is sequestered. Dashed lines show Fe in fluid, and dotted lines show Mg in fluid.

Jarosite-stability method. The water/rock ratio (kg/kg) for the Burns Formation was 10^2 – 10^4 , based on the observation of jarosite (Tosca et al., 2008; Tosca and McLennan, 2009; Hurowitz et al., 2010).³ In this model, pH is lowered by acid produced by dissolving rock, and then oxidizing rock-sourced Fe^{2+} (Hurowitz et al., 2010). Jarosite will not form, and Fe^{3+} -copiapite or rhomboclase will form instead, if the water/rock ratio is $<10^2$ (Tosca and McLennan, 2009) – but jarosite is in fact observed. The implied Burns Formation water/rock ratio of 10^2 – 10^4 is $(3\text{--}300)\times$ that of Andrews-Hanna et al. (2010), who assumed a salinity of 80% that of seawater (i.e., $W/R \sim 40$). For rock density $2500\text{--}2800 \text{ kg/m}^3$ we get a total water demand of $5 \times 10^{20}\text{--}5 \times 10^{22} \text{ kg}$ for the sulfate rocks observed today, i.e. 3–300 km Global Equivalent Layer of water. (This assumes that the bulk of the Burns Formation materials interacted with water, consistent with the paucity of olivine in the Burns Formation.) This increases to 30–3000 km taking account of the now-eroded sulfates entailed by the groundwater hypothesis. Even the lower bound is probably more than can be stored in surface-exchangeable reservoirs in the crust at any one time (Clifford and Parker, 2001). Therefore, this quantity of water strongly suggests a hydrologic cycle between the atmosphere and surface, but does not constrain whether or not this cycle included the deep subsurface.

Cation-supply method. A second, independent constraint on the water demand comes from basalt-water equilibration as calculated using CHIM-XPT simulations (Fig. 3). The CHIM-XPT simulations output dissolved-cation content, dissolved-C content, and pH, all as a function of water/rock ratio. To select Mars-relevant output, we use terrestrial basaltic aquifers as a guide to pH, and then interpolate in the CHIM-XPT output as a function of pH to obtain the corresponding dissolved-cation concentration. We also use the CHIM-XPT output to determine what proportion of C has been precipitated from fluids into carbonate minerals.⁴

³ Throughout this paper, we distinguish between the water:rock ratio computed by dividing the time-integrated water flux by the mass of sulfate-rich rock, and the water:rock ratio of the outlet fluid (which is a measure of the extent of equilibration between groundwater and basalt for each water parcel that upwells to the surface). For example, a water:rock ratio of 1 in CHIM-XPT has total dissolved solids typically $\sim 0.1 \text{ mol/liter}$, so to build up a sulfate deposit containing 10 wt% deep-groundwater-supplied-cations would require a time-integrated water/rock ratio $\gg 1$.

⁴ We do not use the terrestrial basalt aquifer cation and C data directly, in part because Early Mars is thought to have had atmospheric $p\text{CO}_2$ much greater than that of modern Earth.

In order to relate groundwater cation concentrations (mol/liter) output from CHIM-XPT simulations to the water demand (liter) for the sulfate-rich sedimentary rocks, we need to know the cation content (moles) of the sulfate-rich sedimentary rocks. We estimate this in two ways.

a) **Ground-truth approach:** In this approach we use Burns formation measurements as a proxy for sulfate composition (see §5.1 for discussion). According to Squyres et al. (2006), the Burns formation is a mixture of (i) a siliciclastic component that was leached of 55% (by moles) of its divalent cations and (ii) a subsequently-added evaporitic sulfate component; this mixture was subsequently diagenetically modified. This implies that $>3.4 \text{ wt\%}$ of the Burns formation (the Fe in jarosite according to McLennan and Grotzinger, 2008) consists of groundwater-transported Fe, rising to 6.5 wt% for a more involved calculation.⁵ However, Fe is very insoluble in reducing, circumneutral-to-alkaline waters, such as basalt-equilibrated aqueous fluids. The equilibrium concentration of Fe in the fluid is $<0.1 \text{ mmol/liter}$ in CHIM-XPT for $\text{pH} > 7$ and $p\text{CO}_2$ in the range 0.006 bar to 6 bar, i.e. $\lesssim 6 \text{ ppmw}$ (Fig. 3). $p\text{CO}_2 \geq 0.2$ bar is favored for Hesperian Mars, according to climate models (Haberle et al., 2017). This gives a water demand of $\sim 10^{23} \text{ kg}$, i.e. $>500 \text{ km GEL}$ of water, for the $>4 \times 10^5 \text{ km}^3$ of sulfate-bearing sedimentary rock seen today. (A similar argument applies to Ca^{2+} , which is buffered to $<0.04 \text{ mmol/liter}$ in our 0.2 bar basalt calculation, and $<0.003 \text{ mol/liter}$ in our 2-bar calculation.)

b) **Orbital-spectroscopy approach:** Orbital near-infrared spectroscopic data for sulfate-rich rocks outside Meridiani show only occasional evidence for Fe-sulfates, with Mg-sulfates being much more important (e.g. Gendrin et al., 2005; Murchie et al., 2009; Wang et al., 2016). Therefore, we consider the $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ cation endmember, with $n = 2$ to represent a mix of starkeyite and singly-hydrated Mg-sulfate (Wang et al., 2016). We assume Mg-sulfates make up $(40 \pm 20)\%$ of the mass of the sulfate-rich rocks. The corresponding water demand constraint is much looser for Mg-sulfates (i.e., orbital spectroscopy approach) than for Burns-formation composition (i.e., ground truth approach). This is because [Mg] can reach 0.03 mol/liter (i.e. 0.7 g/kg) for the highest $p\text{CO}_2$ levels we investigate (Fig. 3).

4.2. How much C is drawn down per unit water?

The C that is drawn down is the C dissolved in the water at the recharge zone, minus C that reaches the outlet. The difference is due to carbonate formation.

C dissolved in the water at the recharge zone. For water- CO_2 equilibration at 0.01°C , CHIM-XPT outputs $0.39 \text{ mol/liter CO}_{2(\text{aq})}$ at $p\text{CO}_2 = 6 \text{ bar}$, decreasing near-linearly with $p\text{CO}_2$. Thus at 0.6 bar partial pressure, 1.7 CO_2 -equivalent-g/l goes into the water at the recharge zone. This corresponds to 3–5 bars of CO_2 for the 300-to-500-km-thick Global Equivalent Layer of evaporated water that was calculated in §4.1.

C sequestered along the flow-path. What fraction of the initial C in the water in the recharge zone goes into carbonate? CHIM-XPT output shows that C decreases with increasing distance along the

⁵ According to McLennan (2012), Burns formation rock has mean $[\text{SiO}_2]$ of 37.0 wt%. We look up 37.0 wt% SiO_2 in the Sulfur-Plus-Cations (S Addition) worksheet of Data Set S2 (jgre21007-sup-0003-2018JE005718-ds02.xlsx) of McCollom (2018). This gives that 53% of Burns formation Fe consists of groundwater-transported Fe, i.e. 6.5 wt% of the rock. The tab in McCollom (2018) is a quantification of the argument in Squyres et al. (2006). However, Hurowitz and Fischer (2014) state that a lower degree of alteration is consistent with the basic hypothesis of Squyres et al. (2006). We use 3.4 wt% (Fe in jarosite) as a lower bound, and 6.5 wt% as an upper bound.

flow-path, and the amount of sequestration depends on the pH of the water (Fig. 3). Observations (fieldwork and experiment) show $\text{pH} > 7$ for basalt-buffered waters. pH is 9–10 for groundwaters in basalt-buffered aquifers in Iceland, which is consistent with the pH of basalt-buffered fluids in the laboratory when isolated from the atmosphere (Arnórsson et al., 2002). pH for thermal springs in the basaltic Deccan Traps is 8.2 ± 0.5 (Minissale et al., 2000). If the aquifer rock dissolves non-congruently, with preferential dissolution of olivine, then $\text{pH} = 8\text{--}11$ is expected (Kelemen et al., 2011). Drawdown of CO_2 as carbonates in basaltic aquifers has been documented in Iceland (Flaathen et al., 2009), among other locations. In seafloor hydrothermal systems on the flanks of mid-ocean ridges, 80–90% of recharging seawater C can be sequestered as carbonate (Walker et al., 2008).

These results (and their relevance to Mars) can be understood in terms of a ratio of timescales. The flow-through time for a large basaltic aquifer is compared to the dissolution time for rock adjacent to the flow. If the flow time is much more than the dissolution time (i.e. Damköhler number $Da \gg 1$), then the water will be equilibrated with the rock when it reaches the outlet. Darcy's law gives $u = k/\mu \times \Delta p/\Delta x$, where k is the permeability, and $\mu = 10^{-3}$ Pa s is dynamic viscosity of water. Pressure head $\Delta p = \rho \times g \times \Delta z = 10^3 \text{ kg/m}^3 \times 3.7 \text{ m/s}^2 \times 10^4 \text{ m} = 4 \times 10^7 \text{ Pa}$ (here we have conservatively chosen a large Δz), and flow path length $\Delta x = 10^7 \text{ m}$. If we let $k = 10^{-12} \text{ m}^2$, then we obtain $u = 0.01 \text{ m/yr}$. The cross-sectional area of fractures through which the fluid is moving is maybe 1% of the rock volume (\ll the porosity), so the speed of the water is $\sim 100\times$ faster. The flow-through time is $\Delta x/100u = 10^7 \text{ yr}$. 10^7 yr is long enough to dissolve mineral grains (Milliken et al., 2009), and thus to allow minerals and water to reach equilibrium. Thus, as stated in Andrews-Hanna et al. (2010), for “flow timescales on the order of millions of years [...] there is ample time for these fluids to equilibrate with the aquifer matrix.” Thus, deep groundwater should have $\text{pH} 8.2 \pm 0.5$ (or even larger) and $\gtrsim 1/2$ of input C will be sequestered as carbonate (Fig. 3).

4.3. Monte Carlo procedure

The estimates in §4.1 and §4.2 are only rough estimates because many parameters are uncertain. To take account of this uncertainty, we used a Monte Carlo approach. First, to take account of the possibility of incongruent basalt dissolution, we considered dissolution of Mars basalt, and also olivine-only dissolution, as endmembers (Milliken et al., 2009). C_{seq} for these two endmembers is plotted separately in Fig. 4. For each of these two cases, we varied other relevant parameters, as follows. (1) Uncertainty in the original volume of sulfate-bearing sedimentary rocks (V_{sed}) entailed by the global-groundwater hypothesis. We adopt a uniform prior in the range $(2.9\text{--}4.0) \times 10^6 \text{ km}^3$. This sums the present-day outcrop volume of $>3.4 \times 10^5 \text{ km}^3$ (Michalski and Niles, 2012; Hynek and Phillips, 2008); the eroded volume of $0.9\text{--}1.7 \times 10^6 \text{ km}^3$ entailed by the global groundwater hypothesis for Meridiani (Zabrusky et al., 2012); and the eroded volume of $(>1.64) - 2 \times 10^6 \text{ km}^3$ entailed by the global groundwater hypothesis for Valles Marineris (Andrews-Hanna, 2012; Michalski and Niles, 2012). (2) Uncertainty in the sedimentary-rock density ρ_{sed} (uniform prior in the range $2500\text{--}2800 \text{ kg/m}^3$). (3) Uncertainty in the percentage of rock mass corresponding to added Fe (Fe_{added}), ranging from 3.4–6.5 wt% (log-uniform prior, i.e. conservatively favoring smaller values). (4) pH was randomly chosen from the pH measured from 25 thermal springs in the Deccan Traps (Minissale et al., 2000) and 80 low-ground springs in Iceland (Arnórsson et al., 2002). We weighted the random sampling

so that 50% of trials used a Deccan-basaltic-aquifer pH, and 50% of trials used an Iceland-basaltic-aquifer pH. (5) $p\text{CO}_2$ was varied randomly between values of 0.2, 0.6, and 2 bars. We use 0.2 bar as our lower limit; $p\text{CO}_2 < 0.6$ bar will lead to a frozen Mars surface according to existing models (e.g. Haberle et al., 2017). For the jarosite method, we also considered (6) uncertainty in the initial W/R , with a log-flat prior between limits of 10^2 and 10^4 . (Our calculations do not take into account the possibility of surface temperatures $\sim 20^\circ\text{C}$ on Early Mars (Bishop et al., 2018). Such temperatures would reduce both dissolved CO_2 concentrations, and carbonate-mineral solubility). With these assumptions,

$$C_{\text{seq}} \times 10^5 = ([C]_{(\text{pH}, p\text{CO}_2)}^{\text{inlet}} - [C]_{(\text{pH}, p\text{CO}_2)}^{\text{outlet}}) \times W_i \times 0.044 \text{ kg/mol} \times 3.7 \text{ g}$$

where C_{seq} is in bars, and water demand W can correspond to any of our three methods for estimating water demand (§4.1),

$$\begin{aligned} W_{\text{jarosite}} &= (W/R) \rho_{\text{sed}} V_{\text{sed}} \\ W_{\text{Fe}} &= \text{Fe}_{\text{added}} \rho_{\text{sed}} V_{\text{sed}} / [\text{Fe}]_{\text{pH}, p\text{CO}_2} \\ W_{\text{Mg}} &= \text{Mg}_{\text{added}} \rho_{\text{sed}} V_{\text{sed}} / [\text{Mg}]_{\text{pH}, p\text{CO}_2} \end{aligned}$$

where $[\text{Fe}]_{\text{pH}, p\text{CO}_2}$ and $[\text{Mg}]_{\text{pH}, p\text{CO}_2}$ are from calculations like those shown in Fig. 3.

We also plot the “minimum carbonate drawdown” (gray dashed line in Fig. 4). For this we assumed a pH equal to the minimum measured for thermal springs from Deccan by Minissale et al. (2000), i.e. 7.43, and a $p\text{CO}_2$ at the bottom of our range (0.2 bar).

Using the ground-truth approach (i.e. treating *Opportunity* data as representative of sulfate-rich Hesperian sediments), the results show enormous CO_2 drawdown in order to match Fe^{2+} -supply constraints (Fig. 4). Indeed, CO_2 drawdown is much greater than plausible Hesperian CO_2 sources, beginning-of-Hesperian $p\text{CO}_2$, or the sum of the two (Stanley et al., 2011; Kite et al., 2014). The implication is that Mars' atmosphere would have been driven underground. Since an atmosphere is required in order to warm the climate enough to prevent formation of a global cryosphere and thus allow global groundwater circulation, this hypothesis undermines itself. However, this result does not by itself disprove the hypothesis of global groundwater circulation. For example, using the orbital spectroscopy approach (i.e. approximating the sulfate component of the sulfate-rich rocks as being exclusively Mg-sulfates), the CO_2 drawdown is much less (Fig. 4). The 90% range of uncertainty for CO_2 drawdown includes some that are small enough to be consistent with existing data. There are other workarounds and alternatives, as we now discuss.

5. Discussion

5.1. Rescue for the global-groundwater hypothesis?

There are several work-arounds for the global groundwater circulation hypothesis that can improve the agreement between $p\text{CO}_2$ constraints and CO_2 drawdown. We list these below, from the least likely to (in our judgment) the most likely:

(a) *Overestimated V_{sed}* ? This work-around posits that the volume of sulfate-bearing outcrop seen today is not much less than the pre-erosion volume. This may be true (e.g. Michalski and Niles, 2012; Kite et al., 2013b), but is hard to square with the hypothesis that the engine of formation for sulfates was a global groundwater circulation. Suppose that the present-day mounds formed via upwelling of deep-sourced groundwater and had a maximum volume not much more than their present-day volume. Then, given the topographic isolation of the present-day mounds, the corollary

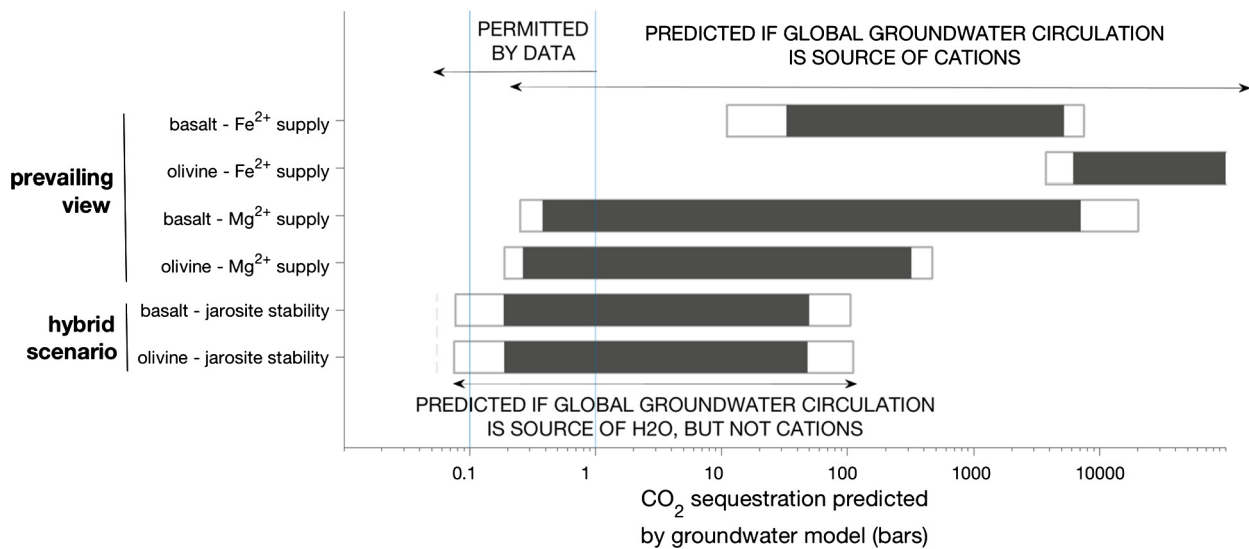


Fig. 4. CO₂ sequestration. The dark gray bars show the 90% range of uncertainty and the light gray boxes show the 99% range of uncertainty, both as output from the Monte Carlo procedure described in the text. The blue line shows the upper limit of outgassed CO₂. The thin dashed gray lines show the lowest values permitted by the jarosite stability calculation. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

is that the mounds are spring mounds. This is unlikely based on structural geology analysis (e.g. Kite et al., 2016).

(b) *The atmosphere at the start of the Hesperian was very thick, and/or volcanoes outgassed >10 bars of CO₂ during the Hesperian.* This is unlikely. For example, lab experiments, Mars-meteorite-based redox estimates, and geologic constraints on the volume of post-3.6 Ga magmatism, suggest only <0.1 bar was released into the atmosphere during the Hesperian (Stanley et al., 2011; Grott et al., 2011).

(c) *Waters did not equilibrate with the Hesperian atmosphere.* In this picture, basal melting of glaciers recharges the aquifers. Because ice traps <100 ppmw air, the basal ice-melt water holds little C. This hypothesis is in tension with models of ice flow on Early Mars, which predict little or no basal melt (Kite and Hindmarsh, 2007; Fastook and Head, 2015). Another way to avoid equilibration between groundwater and the Hesperian atmosphere is “one-shot” upwelling-from-depth of very saline groundwater. Highly saline waters could be sourced by dissolution of buried Noachian sulfates (Zolotov and Mironenko, 2016), or infiltration of water from a primordial ocean.

(d) *Later waters flowed through fractures coated with carbonate precipitated from earlier waters, so that later waters arrived at the evaporation zone without having equilibrated with basalt.* This work-around predicts that waters upwelling at Meridiani would have been equilibrated with carbonate. If so, carbonate precipitation would have occurred at Meridiani. However, carbonate is not observed in the Burns formation. Therefore this work-around is unlikely.

(e) *Carbonate recycling by acid weathering, or thermal breakdown of carbonates by heat from lava.* In this work-around, carbonates do form, but at depths shallow enough for subsequent dissolution by volcanogenic H₂SO₄ or (in the case of Tharsis recharge) by heat from overlying lava (Glotch and Rogers, 2013). This recycles CO₂ back into the atmosphere.

(f) *Rocks seen by Opportunity have elemental compositions that are not representative of Hesperian sulfates on Mars.* (This is essentially the “Orbital spectroscopy” approach, corresponding to the Mg²⁺ supply constraint in Fig. 4). Orbiter infrared spectroscopy shows association of Fe-oxides and sulfates (e.g. Bibring et al., 2007) – the “Laterally Continuous Sulfate” orbital facies of Grotzinger and Milliken (2012) which includes much of Meridiani, Valles Marineris and nearby chaos, and Gale crater, among other sites. However, Mars orbiter visible-and-near-infrared spectroscopy cannot pre-

cisely constrain bulk rock Fe content, and Mars orbiter gamma ray spectroscopy (which can measure bulk rock Fe content) does not resolve Hesperian sulfate-rich bedrock outcrops. Therefore, it is not known whether or not rocks seen by Opportunity have sulfate cation compositions that are typical of Hesperian sulfates on Mars. Fortunately, *Curiosity* will soon arrive at sulfate-rich rocks in Gale, 8000 km from Meridiani, and test the hypothesis that sulfate-rich Hesperian rocks are similar around the planet. If the Burns formation is unusually rich in Fe-sulfates and secondary Fe-oxides, then the global-groundwater circulation hypothesis predicts that the dominant cation transported is Mg-sulfate, with 100× smaller concentrations of Fe and Ca (Fig. 3; Wang et al., 2016).

(g) *Waters from the deep subsurface were not a major source of cations for the sulfates; instead, cations were leached from wind-blown siliciclastic material.* Thus, cation vertical transport distance in aqueous solution (including late-stage remobilization, e.g. of MgSO₄) was <<1 km. Deep-sourced groundwater is not the source of the extra cations in the “added sulfates” at Meridiani or elsewhere.

We refer to this work-around as the “hybrid scenario”. It corresponds to the lowest two rows in Fig. 4, and the central panel in Fig. 5. In this work-around, almost none of the cations for the sulfates are derived from deep-sourced groundwater. Instead, deep-sourced groundwater provides only a small fraction of the Fe²⁺ (or Ca²⁺), but almost all of the H₂O. This allows the water:rock ratio to be as low as compatible with jarosite stability; i.e., 100:1 (Hurowitz et al., 2010). In the hybrid scenario, Fe oxidation creates acidity that may have allowed modest additional leaching of rocks immediately beneath the Burns formation (e.g. the Shoemaker formation). If the cations do not come from deep-sourced groundwater, where else could they come from? In the hybrid scenario, the build-up of the evaporitic sandstone is rate-limited by the supply of wind-blown material. Without wind-blown material, there are almost no cations and thus almost no sulfates. If this is true, then no “clean” sulfate evaporites will be found on Mars: in other words, Martian sulfates are necessarily dirty.⁶ This can be tested by *Curiosity*’s imminent exploration of sulfate-rich rocks at Gale crater.

The hybrid scenario (g) permits the global groundwater circulation hypothesis to match data. However, if the deep-sourced

⁶ With hindsight, this may explain the non-detection of a clean playa-lake deposit along *Opportunity*’s traverse.

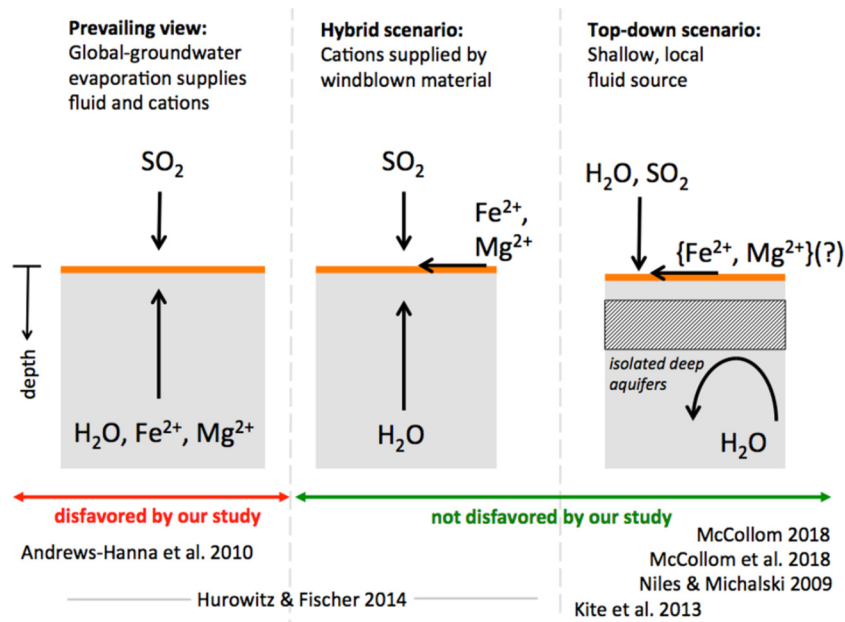


Fig. 5. Summaries of 'prevailing view,' 'hybrid scenario,' and 'top-down scenario' for formation of sulfates hosted in the sedimentary rocks of Hesperian Mars.

groundwater is not the source of the salinity in the evaporites at Meridiani, then there is no longer a geochemical rationale for appealing to deep-sourced groundwater. Water on Mars does not have to come from below, as we now discuss.

5.2. Alternatives to the global-groundwater hypothesis

Sulfates can form by reaction between sulfuric acid and olivine at ultracold temperatures (e.g. Niles and Michalski, 2009; Niles et al., 2017). The possibility that this process was the engine of sulfate formation at Meridiani is not ruled out by bulk geochemical data. Indeed, it has been proposed that Burns formation bulk geochemistry can be explained by S/SO₂ addition only, with no need for extra cations (McCullom, 2018, and references therein). Addition of S/SO₂ alone, without cation addition, accounts for the lack of evidence at Meridiani for Na, K, and Si mobility. This lack of mobility is inconsistent with the expectation that these elements should be mobilized along with Fe and Mg (McCullom, 2018; and our CHIM-XPT output, see Supplementary Information). This S-added scenario is an alternative to the view of the Mars Exploration Rover team, which is that Burns formation bulk geochemistry is the result of addition of both S and cations (Squyres et al., 2006; Hurowitz and Fischer, 2014; Cino et al., 2017). Indeed, the totality of the textural, compositional and stratigraphic data requires movement of groundwater at >1 m vertical and >100 m horizontal scale (Grotzinger et al., 2005; McLennan et al., 2005). This textural evidence is not incompatible with the idea that the sulfates themselves were formed by reaction between SO₂ and basalt: perhaps the bulk geochemistry is set by S/SO₂-addition, with later modification (hematite concretion formation, perhaps MgSO₄-mobilization) by groundwater. In future, instruments that tie geochemistry to texture at sub-mm scale will be useful to resolve the ambiguity of bulk geochemical analysis – e.g., the Planetary Instrument for X-ray Lithochemistry (PIXL) on Mars 2020 (Allwood et al., 2015). In the meantime, our calculations, by themselves, can be reconciled with both the salt-added and S-added views (Fig. 5). (In Fig. 5, only a single, atmospheric source for SO₂ is indicated, for simplicity. An atmosphere-derived contribution to Mars S is indicated by isotope data; Franz et al., 2017.

FeS₂-derived S could also contribute to the sulfates; Dehouck et al., 2012.)

Global groundwater circulation was originally proposed in part to resolve the recognized conundrum of sulfate build-up at Meridiani in the absence of a closed topographic basin. This conundrum is addressed in the global groundwater circulation model (Andrews-Hanna et al., 2010). Alternative solutions to the conundrum exist – one example is the “flypaper” model (Kite et al., 2013a). In the “flypaper” model, on 10^{8–9} yr timescales, wind-blown material is abundant, and migrates globally. Windblown sediments can undergo acid leaching and aqueous cementation, but only where surface water is available. Surface water is only available (according to the model of Kite et al., 2013a) in locations where snowpack can seasonally melt. Seasonal meltwater has an expected Gyr-integrated spatial distribution (for a Mars climate on the cusp of final dry-out) that is a good match for the observed spatial distribution of light-toned sedimentary rocks (Kite et al., 2013a). In this model, the spatial distribution of light-toned sedimentary rocks corresponds to zones of past seasonal snowmelt, and the snowmelt acted as “flypaper” that trapped windblown material.

5.3. Linking cation composition, carbon isotopes, and climate change

It is interesting that our central estimate of atmospheric draw-down (C_{seq}) is so large, even for the hybrid scenario (Fig. 4). If global groundwater circulation did operate (Fig. 5), then it is likely that carbonate sequestration was the principal sink for CO₂ at times when global groundwater circulation was active during the Hesperian – faster than escape-to-space (Jakosky et al., 2018). This hypothesis might be tested at Mt. Sharp with *Curiosity* logging of $\delta^{13}\text{C}$. Measurements indicating a decrease in atmospheric $\delta^{13}\text{C}$ during the interval of sulfate formation would be consistent with carbonate sequestration as the dominant sink for CO₂ during the Hesperian (e.g., Hu et al., 2015). This is because ¹³C is preferentially incorporated in the carbonate, and some of the lightened C survives to the zone of upwelling (Fig. 3).

Moreover, our analysis links *Curiosity* measurements of cation content at Mt. Sharp to the prevailing view that evaporation of water from global groundwater circulation provided both cations

and water for the sulfates. *Curiosity* detection of Fe-sulfates or abundant Fe-oxides would further disfavor the prevailing view (Figs. 4–5). On the other hand, *Curiosity* detection of Mg-sulfates with no secondary Fe-minerals could be consistent with the prevailing view (Fig. 4).

6. Summary and conclusions

We quantify the “carbon tax” for a global hydrologic cycle including deep groundwater (recharge → deep aquifers → evaporation → recharge) on Hesperian Mars. We find that if deep-sourced groundwater is the source of the cations needed to explain the mineralogy of the sulfate-rich rocks, then the CO₂ sequestration is >0.3 bars (>30 bars if the Fe-contents measured by *Opportunity* ground-truth are representative of sulfate-rich Hesperian layered sediments). These are conservative estimates, because pH > 8 waters, expected for long flow paths, can transport even fewer cations per unit CO₂ sequestration. This increases the “carbon tax.” Our central estimates of CO₂ sequestration (as carbonate) are all well in excess of available CO₂ (Fig. 4). This tension does not arise for alternatives to the global groundwater circulation hypothesis, such as a top-down water supply (e.g. Kite et al., 2013a). This tension also does not arise for a ‘hybrid’ scenario where deep-sourced groundwater provides dilute fluids, and cations are brought in by windblown material (Fig. 5).

All these CO₂-drawdown numbers are large enough to affect climate. Therefore, a global groundwater circulation that could extend Mars surface habitability on a drying planet (e.g., Andrews-Hanna and Lewis, 2010) would contribute to its own demise. The low end of this CO₂ sequestration range is not ruled out by the data, and predicts a Hesperian downward trend in $\delta^{13}\text{C}$ that is potentially testable by *Curiosity*. Our work does not disprove the hypothesis of global groundwater circulation on Hesperian Mars. Our results suggest potential problems with (and new tests for) the geochemical justification for the hypothesis of global groundwater circulation on Hesperian Mars.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.epsl.2019.115718>.

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