

Low Hesperian P_{CO_2} constrained from in situ mineralogical analysis at Gale Crater, Mars

Thomas F. Bristow^{a,1}, Robert M. Haberle^b, David F. Blake^a, David J. Des Marais^a, Jennifer L. Eigenbrode^c, Alberto G. Fairén^d, John P. Grotzinger^e, Kathryn M. Stack^f, Michael A. Mischna^f, Elizabeth B. Rampe^g, Kirsten L. Siebach^e, Brad Sutter^h, David T. Vanimanⁱ, and Ashwin R. Vasavada^f

^aExobiology Branch, NASA Ames Research Center, Moffett Field, CA 94035; ^bPlanetary Systems Branch, NASA Ames Research Center, Moffett Field, CA 94035; ^cSolar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, MD 20771; ^dDepartment of Planetology and Habitability, Centro de Astrobiología, Madrid 28850, Spain; ^eDivision of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125; ^fJet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109; ^gAstromaterials Research and Exploration Science Division, NASA Johnson Space Center, Houston, TX 77058; ^hJacobs Technology, Inc., NASA Johnson Space Center, Houston, TX 77058; and ⁱPlanetary Science Institute, Tucson, AZ 85719

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Carbon dioxide is an essential atmospheric component in martian climate models that attempt to reconcile a faint young sun with planetwide evidence of liquid water in the Noachian and Early Hesperian. In this study, we use mineral and contextual sedimentary environmental data measured by the Mars Science Laboratory (MSL) Rover *Curiosity* to estimate the atmospheric partial pressure of CO_2 (P_{CO_2}) coinciding with a long-lived lake system in Gale Crater at ~ 3.5 Ga. A reaction–transport model that simulates mineralogy observed within the Sheepbed member at Yellowknife Bay (YKB), by coupling mineral equilibria with carbonate precipitation kinetics and rates of sedimentation, indicates atmospheric P_{CO_2} levels in the 10s mbar range. At such low P_{CO_2} levels, existing climate models are unable to warm Hesperian Mars anywhere near the freezing point of water, and other gases are required to raise atmospheric pressure to prevent lake waters from being lost to the atmosphere. Thus, either lacustrine features of Gale formed in a cold environment by a mechanism yet to be determined, or the climate models still lack an essential component that would serve to elevate surface temperatures, at least locally, on Hesperian Mars. Our results also impose restrictions on the potential role of atmospheric CO_2 in inferred warmer conditions and valley network formation of the late Noachian.

Hesperian Mars | martian atmosphere | Mars Science Laboratory | Gale Crater | carbon dioxide

More than four decades of orbital imaging of Mars provide geomorphological evidence of a more active hydrological cycle and larger inventory of water during the Noachian and Early Hesperian (1, 2). The widespread distribution of hydrous clay minerals in martian terrains of this age and their subsequent demise provide pivotal supporting evidence (3, 4), but the clay mineral-bearing deposits also present a paradox in that carbonate minerals, expected coprecipitates in surficial settings in communication with a CO_2 -bearing atmosphere, are typically absent (5). Atmospheric reconstructions using carbon isotopic measurements and global inventories of martian carbon also indicate 100s mbar CO_2 levels (5, 6). This leads to the question of how the surface of ancient Mars, faintly heated by a young sun, was kept warm enough to allow an active hydrological cycle, without substantial amounts of a key greenhouse gas in the atmosphere. However, the breadth of available constraints on carbon sinks (6) and potential clay mineral formation in subsurface settings uninfluenced by the atmosphere (7) introduce uncertainties to estimates and the periods to which they apply. In this work we use mineralogical and sedimentological data from ~ 3.5 Ga martian lake sediments to obtain a reference point for the evolution of martian P_{CO_2} .

During its traverse to the lower slopes of Aeolis Mons (informally known as Mt. Sharp), the MSL team documented a ~ 70 m sedimentary section of mudstones, siltstones, sandstones, and conglomerates deposited by lakes and rivers on the floor of Gale crater between 3.8 and 3.1 Ga (8). Sedimentary rocks analyzed by the

CheMin X-ray diffraction (XRD) instrument during the traverse share many of the same components including (i) crystalline silicates including pigeonite, intermediate calcic plagioclase, and olivine from a basaltic source or sources; (ii) poorly crystalline clay minerals; (iii) various Fe oxides including magnetite; (iv) Ca–sulfate minerals, which mainly occur in cross-cutting fractures and veins; and (v) an X-ray amorphous component (9, 10). Thus far, carbonate minerals have not been definitively detected in Gale Crater sedimentary rocks. This is surprising given the reactivity of minerals making up sediments to carbonic acid.

Of the phases present, smectitic clay minerals and magnetite provide a potential means of estimating ancient P_{CO_2} by constraining dissolved inorganic carbon (DIC) levels in the pore fluids of Gale Crater sediments. It is proposed that isochemical alteration during the deposition of lacustrine mudstone at YKB involved dissolution of Fe^{2+} -bearing olivine (Fo_{62}) providing a source of Fe^{2+} and Mg^{2+} in pore waters for subsequent coeval precipitation of magnetite and Fe^{2+} -bearing, ferrian saponite-type clay minerals (9, 11–14). The detection of these secondary phases indicates anoxic to poorly oxidizing conditions (13), and places lower limits on the pore water activity of Fe^{2+} and Mg^{2+} released from olivine. Therefore, the thermodynamic stability fields of ferrian saponite and magnetite with respect to Fe and Mg carbonates can be used as the basis of estimates of atmospheric P_{CO_2} at the time of Sheepbed deposition. Ferrian saponite and magnetite are thermodynamically unstable with respect

Significance

Approximately 3.5-Ga sedimentary rocks surveyed by the Mars Science Laboratory rover in Gale Crater, Mars, contain secondary mineral phases indicating aqueous alteration and release of cations from mafic minerals during sediment deposition in lakes. However, carbonate phases are not detected, and our model calculations indicate atmospheric CO_2 levels at the time of sediment deposition 10s to 100s of times lower than those required by climate models to warm early Mars enough to maintain surficial water. Our results offer a ground-based reference point for the evolution of martian atmospheric CO_2 and imply that other mechanisms of warming Hesperian Mars, or processes that allowed for confined hydrological activity under cold conditions, must be sought.

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¹To whom correspondence should be addressed. Email: thomas.f.bristow@nasa.gov.

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to Fe and Mg carbonates, such as siderite and magnesite, between 10^{-5} to 10^{-2} bar P_{CO_2} depending on assumed activity of silica and Al^{3+} of pore waters (Fig. 1).

Estimates of P_{CO_2} on the Archean (>2.5 Ga) Earth, derived from paleosols and banded iron formations, also use the thermodynamic stability of clay minerals and magnetite (17–19), but are criticized because they rely on assumptions of mineral equilibrium and do not account for enhanced delivery of carbon and reducing power to sediments via biological activity (20, 21). Metamorphic overprinting of original mineral assemblages in terrestrial rocks this old is ubiquitous and complicates interpretations further (22).

In many ways, deriving P_{CO_2} estimates from Gale Crater sedimentary rocks is more straightforward than doing so in their terrestrial equivalents. Examination of ancient sediments at YKB shows that they, despite their age, have been subject to minimal burial diagenetic alteration and heated to no more than 70 °C (9, 12, 13) consistent with reconstructed burial history and estimates of ancient geothermal gradients (23). The observed persistence of smectite clay minerals, magnetite, levels of hematite at CheMin's detection limit of ~1 wt % and absence of cation leaching in YKB sediments revealed by bulk geochemistry (9, 11) is inconsistent with pervasive postdepositional chemical weathering or alteration that may have otherwise had the potential to dissolve authigenic carbonate minerals.

In addition, MSL has not detected signs of biological influence on the Gale Crater sediments. In particular, the organic molecules observed by the Sample Analysis at Mars (SAM) instrument suite are extremely localized and restricted to simple structures

(e.g., C1-C4 alkyl and single-ring aromatic hydrocarbons and chlorohydrocarbons; ref. 24) that lack source information. As such, they may be derived from meteoritic, abiogenic, or geologically reworked biological inputs to the sediments.

Assuming that sedimentary mineral assemblages were in thermodynamic equilibrium with the atmosphere remains problematic, however. Even with martian P_{CO_2} levels above thermodynamic thresholds for carbonate stability, notoriously slow precipitation kinetics of Fe and Mg carbonates may have been a barrier to producing detectable quantities in Gale Crater sediments before burial and isolation from an atmospheric carbon source. For example, magnesite requires temperatures greater than ~70 °C for direct precipitation in the laboratory (25). Siderite forms under ambient laboratory conditions at rates ~4 orders of magnitude slower than calcite (26).

Here we take a step beyond assuming mineral equilibrium and combine estimated sedimentation rates, afforded by detailed sedimentary facies analysis (8, 12), with carbonate precipitation kinetics and observed mineralogy to estimate ancient P_{CO_2} using a geochemical reaction–transport model.

Model Summary

Our models are constructed to determine threshold P_{CO_2} levels that would permit the precipitation of detectable amounts of siderite by CheMin. For samples bearing the mixture of phases observed within Sheepbed mudstone (9), CheMin has a detection limit of ~1 wt % siderite. The SAM instrument detects release of CO_2 upon sample heating, which can, in part, be derived from decomposition of carbonate minerals. The results of SAM analyses of YKB sediments provide no clear indication of Fe carbonate, but the expected CO_2 signal for carbonates may be masked by other CO_2 sources thus permitting the presence of Fe carbonates at abundances below the CheMin detection limit (27).

Precipitation rates and therefore accumulation of carbonates depend on the saturation state of pore water with respect to a particular carbonate phase (Ω), given by

$$\Omega_{\text{carbonate}} = \frac{[\text{M}^{2+}][\text{CO}_3^{2-}]}{[K_{\text{sp}}]}, \quad [1]$$

where K_{sp} is the solubility product of the carbonate in question and M^{2+} represents the concentration of the metal cation in pore water.

Ω is linked to carbonate precipitation rate (R_{carbprec}) by the expression,

$$R_{\text{carbprec}} = K_{\text{carbprec}}(\Omega_{\text{carbonate}} - 1)^n, \quad [2]$$

where K_{carbprec} is the rate constant and n is the order of the reaction.

Our models calculate $[\text{CO}_3^{2-}]$ by simulating advection, diffusion, and reaction of DIC species, including precipitation of carbonate, in a one-dimensional porous sedimentary profile subject to active sedimentary accumulation and burial (detailed in *SI Text, Model Details*). Diffusion and advection from the upper model boundary actively replenish DIC (including CO_3^{2-}) lost from pore waters during carbonate precipitation and transport and, thus, are of critical importance in modeling the total carbonate accumulation. Upper model boundary conditions are set to simulate a well-mixed lake in equilibrium with an assigned P_{CO_2} atmosphere. This is a valid representation given the absence of glaciogenic sedimentary features, such as dropstones, ice wedges, and glacial tills, in Gale lake deposits that would indicate ice cover, and the meter-scale thicknesses of delta deposits that indicate water depths of the same order (8).

We can make broad inferences about lake water chemistry at the time of YKB formation deposition. Salinity appears to have been low based on limited Cl and S concentration in the sedimentary

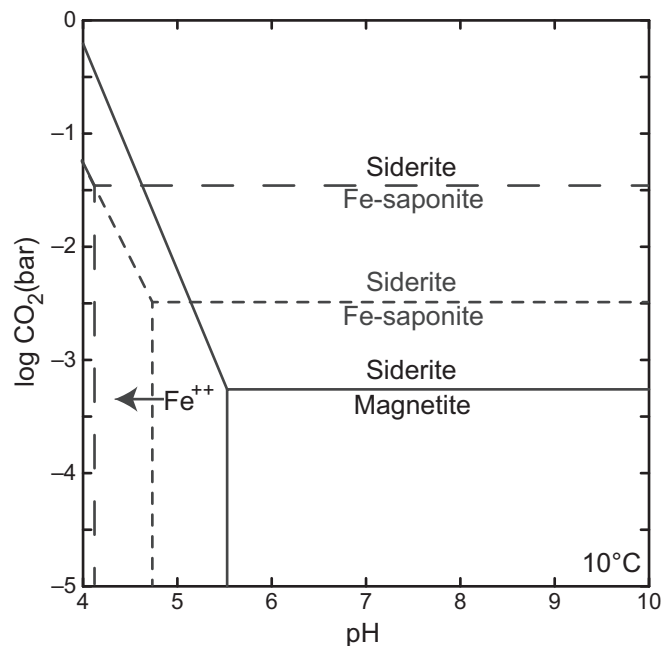


Fig. 1. Thermodynamic stability of secondary minerals (magnetite and Fe saponite) detected in the Sheepbed member, Yellowknife Bay with respect to siderite under varying pH and gaseous CO_2 levels. The threshold P_{CO_2} at which siderite is favored over ferrian saponite is dependent on aqueous silica and Al^{3+} activity. The threshold is higher when $\text{SiO}_{2(\text{aq})}$ is saturated with respect to amorphous silica (long dashed line) rather than quartz (short dashed line). In both cases Al^{3+} is set to saturation with respect to albite—reasonable given that the Sheepbed contains ~20 wt % plagioclase feldspar (9). In drawing the stability boundaries for magnetite, redox state is set at the magnetite/hematite boundary, as detailed in the main text. All thermodynamic data come from the Lawrence Livermore National Laboratory dataset (15) with the exception of Fe saponite ($\text{Na}_{0.35}\text{Fe}_3\text{Al}_{0.35}\text{Si}_{3.65}\text{O}_{10}\text{OH}_2$) determined by Wilson et al. (16). Diagram produced using Geochemist Work Bench 9.

profiles more efficient, lowering P_{CO_2} thresholds. Because we aim to determine an upper constraint on P_{CO_2} we focus our discussion on the P_{CO_2} thresholds obtained assuming pH of lake waters between 5 and 7—the lowest values compatible with saponite and magnetite precipitation (Fig. 1).

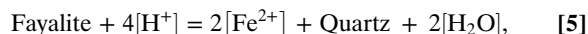
Sedimentary porosity influences the rates of siderite production by controlling the quantity of pore water DIC available for reaction with Fe^{2+} released from olivine and rates of chemical diffusion within sediments, both of which generally increase with porosity. On Earth, mud deposits typically have initial porosities of between 60 and 80% (31). We have assigned a porosity value of 60% in our model profiles to obtain upper P_{CO_2} thresholds (Fig. 24). No significant sedimentary compaction is expected within ~1.5–3 m model interval where carbonates form.

Calculated P_{CO_2} thresholds are also highly sensitive to sediment accumulation rates, with faster rates permitting higher threshold atmospheric P_{CO_2} levels (Fig. 2). We have no direct constraints on the rates of deposition of the YKB formation, but given the similarity of the sedimentary architecture with terrestrial fluvial-lacustrine deposits (8) we use compilations of thousands of lacustrine accumulation rates observed on Earth to obtain an upper limit for the YKB formation (31). Terrestrial lacustrine sedimentation rates span several orders of magnitude, with a dependence on the time span of accumulation (32). With accumulation times of 100s to 10,000 y estimated for the 1.5-m-thick Sheepbed member (12), accumulation rates as high as 5 cm/y are possible, with an average rate ~0.1 cm/y (32). Lacustrine deposits with sedimentation rates >1cm/y make up <1% of available records. The highest rates are not sustainable for periods of more than ~100 y, thus we use an upper sedimentation rate of 1 cm/y in calculating P_{CO_2} estimates. We find that temperature and pore water salinity have a minor influence on P_{CO_2} thresholds (Fig. 2B; *SI Text, Sensitivity Tests*).

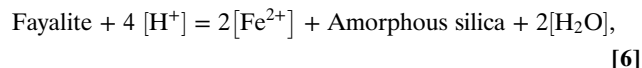
At 10 °C and a salinity of 10 g/kg, an accumulation rate of 1 cm/y and sedimentary porosity of 60% the upper limit on P_{CO_2} levels where siderite production remains below XRD detection limits in the Sheepbed member is 70 mbar. This falls to 10 mbar at average sedimentation rates of ~0.1 cm/y. Our P_{CO_2} estimates are orders of magnitude above those based on thermodynamic stability of magnetite with respect to siderite (Fig. 1), but remain well below the 1000s mbar CO_2 levels required by the most optimistic climate simulations to keep the average temperature

of early Mars above 273 K for long periods (33); for example, Ramirez et al. (34) model clement conditions at 1.3 bars CO_2 , with 20% H_2 as an additional greenhouse gas.

As discussed above, our models and choice of input parameters are designed to provide an absolute upper limit P_{CO_2} based on observed mineralogy and sedimentology at YKB. However, there are various reasons to believe that $[\text{Fe}^{2+}]$ was higher in pore waters and P_{CO_2} may have been lower than the thresholds shown in Fig. 2. First, it is possible that magnetite and hematite detected in YKB sediments (9) are detrital phases that do not place bounds on pore water $[\text{Fe}^{2+}]$ or act as a sink for Fe. This would allow for more reducing conditions, higher $[\text{Fe}^{2+}]$ (Fig. S2) and lower P_{CO_2} thresholds. Second, if the supply of $[\text{Fe}^{2+}]$ from olivine outstripped removal by secondary phases (i.e., olivine dissolution kinetics >> precipitation of secondary phases), $[\text{Fe}^{2+}]$ would also be higher than in our upper threshold P_{CO_2} simulations. In both these cases $[\text{Fe}^{2+}]$ would tend toward approaching levels of olivine saturation, thus providing a reduced P_{CO_2} threshold limit for a given sedimentation rate, porosity, salinity, and temperatures. Model $[\text{Fe}^{2+}]$ for this lower P_{CO_2} threshold based on olivine saturation requires an assumption about $[\text{SiO}_{2(\text{aq})}]$ of pore waters to be made, but in natural near-surface pore waters $[\text{SiO}_{2(\text{aq})}]$ is typically between saturation with respect to quartz or amorphous silica. Both these situations can be used to obtain a pH-dependent expression to determine $[\text{Fe}^{2+}]$:



or



$$[\text{Fe}^{2+}] = \sqrt{K_{\text{reaction}} \cdot [\text{H}^+]^4}, \quad [7]$$

where K_{reaction} is the reaction constant of either Eq. 5 or 6. The resulting P_{CO_2} thresholds are shown in Fig. 3. With comparable porosity and burial rates P_{CO_2} thresholds are approximately half the values calculated assuming pore water $[\text{Fe}^{2+}]$ at magnetite saturation. This reinforces our estimates that the martian atmosphere contained 10s mbar levels at the time of deposition of YKB sediments.

Fluvial-lacustrine sediments in Gale Crater represent one of the youngest known instances of habitable surficial aqueous conditions on Mars, on the tail end of a period of rapid atmospheric degradation and loss (6, 12, 33). Thus, our P_{CO_2} estimate serves as a reference point at a critical juncture in martian atmospheric evolution. Combining ~10s mbar estimates of P_{CO_2} derived from Gale Crater with upper estimates of the amount of CO_2 lost through sequestration as carbonate minerals in the martian crust (up to ~500 mbar CO_2 ; ref. 35) and CO_2 lost to space (<100 mbar; ref. 36) limits atmospheric CO_2 during the Noachian and Early Hesperian to 100s mbar. This is well below threshold levels required to keep the average temperature of early Mars above 273 K for long periods in climate models, therefore either lacustrine features of Gale formed in a cold environment (37) or the problem of reconciling Mars' early climate with geological record of an active hydrosphere remains. Our results imply that the overall lack of carbonates found in the geological record of Mars (5, 6, 28, 35) is a direct reflection of the composition of the ancient atmosphere.

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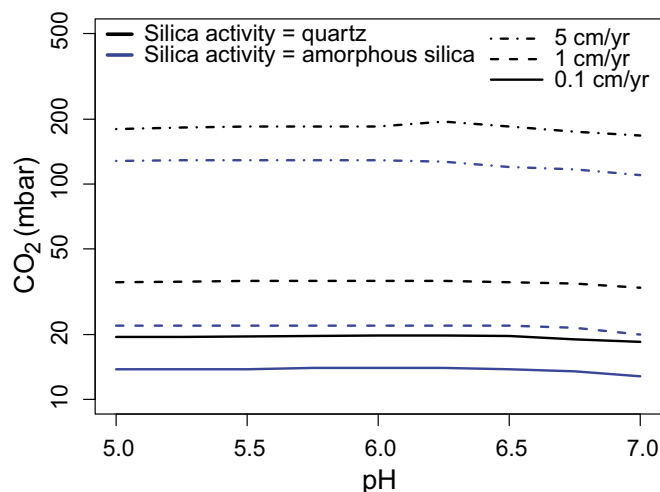


Fig. 3. P_{CO_2} required to produce 1 wt % siderite within model sedimentary profiles at various sediment accumulation rates, sediment porosities, and water column pH values. $[\text{Fe}^{2+}]$ is set at equilibrium with fayalite with silica saturation in equilibrium with quartz (black lines) and amorphous silica (blue lines). Sedimentary porosity is set at 0.6 in all simulations.

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