Semiarid climate and hyposaline lake on early Mars inferred from reconstructed water chemistry at Gale

Keisuke Fukushi¹*, Yasuhito Sekine¹,2, Hiroshi Sakuma³, Koki Morida⁴ & Robin Wordsworth⁵

Salinity, pH, and redox states are fundamental properties that characterize natural waters. These properties of surface waters on early Mars reflect palaeoenvironments, and thus provide clues on the palaeoclimate and habitability. Here we constrain these properties of pore water within lacustrine sediments of Gale Crater, Mars, using smectite interlayer compositions. Regardless of formation conditions of smectite, the pore water that last interacted with the sediments was of Na-Cl type with mild salinity (~0.1–0.5 mol/kg) and circumneutral pH. To interpret this, multiple scenarios for post-depositional alterations are considered. The estimated Na-Cl concentrations would reflect hyposaline, early lakes developed in $10^{4}$–$10^{6}$-year-long semiarid climates. Assuming that post-depositional sulfate-rich fluids interacted with the sediments, the redox disequilibria in secondary minerals suggest infiltration of oxidizing fluids into reducing sediments. Assuming no interactions, the redox disequilibria could have been generated by interactions of upwelling groundwater with oxidized sediments in early post-depositional stages.
There have been a number of attempts to estimate water chemistry (i.e., pH, salinity, redox state, and dissolved species) on early Mars by means of geochemical reaction-transport modeling. These bottom-up modeling approaches can reproduce time and spatial variations of water chemistry based on the observed mineral assemblages. However, they need to assume initial solution compositions, reactant minerals, fluid permeability, water-rock ratios, and a series of chemical reactions. Thus, these studies involve a number of uncertainties depending on these a-priori parameters, which are always difficult to constrain on early Mars.

In contrast, a top-down approach for quantitative reconstruction of water chemistry of pore water in terrestrial clay-bearing rocks has been proposed by Gaucher et al. Using the mineralogical and chemical compositions of clay-bearing rocks and their cation exchange equilibria, this approach successfully reproduces the water chemistry of terrestrial pore waters without any a-priori parameters. Smectite is unique in possessing exchangeable cations in interlayer sites. Although there is a wide diversity of mineralogical characteristics of smectites including the chemical compositions and formation processes, all smectites possess the cation exchange capacity (Supplementary Fig. 1). The cation exchange reaction of smectite is very rapid process with...
fractures strongly suggests that the post-depositional fluids provided additional $\text{SO}_4^{2-}$ into the sediments in the last wetting event.\textsuperscript{11,16} If the post-depositional $\text{SO}_4^{2-}$-rich fluids infiltrate into smectite-rich matrix of the sediments, the primary evaporites left in the matrix would have been re-dissolved and mixed with the additional components (Fig. 1d). The duration of the last wetting event determines whether the post-depositional fluids infiltrate into the matrix. Using both terrestrial analog permeability of dried marine clays (10$^{-7}$–10$^{-10}$ cm/s)\textsuperscript{20} and the typical distance between the calcium sulfate fractures in the Yellowknife Bay sediments (~1 cm)\textsuperscript{11}, post-depositional fluids can chemically interact with the matrix of the Yellowknife Bay sediments in a wetting event for 1–10$^2$ years or longer through diffusion.

Here we apply the top-down approach\textsuperscript{4} to the Yellowknife Bay sediments at Gale Crater, Mars. To quantitatively estimate the water chemistry of the pore water that finally interacted with the sediments, we use the exchangeable cation compositions of smectite's interlayer together with the presence of secondary minerals commonly found in Yellowknife Bay (see Methods). Our results show that the pore water is characterized as mildly saline, Na–Cl type water. We interpret that this salinity of the pore water originates from lake water trapped within sediments in early Gale lakes. The salinity of the lake water would have provided through hydrological cycles during warm and semiarid climate periods in the Hesperian.

**Results and Discussion**

Based on the hydrogeological context (Fig. 1), we consider two end-member scenarios concerning the interactions between the primary and additional components in the sediments (see Methods): In one, the post-depositional $\text{SO}_4^{2-}$-rich fluids in the last wetting event fully interact with the sediments (the full-interaction scenario), while in the other we assume no chemical interactions between the post-depositional $\text{SO}_4^{2-}$-rich fluids and the sediments in the last wetting event (the no-interaction scenario; Fig. 1e). In the full-interaction scenario, we consider that the pore water was reacted with not only the primary components in the matrix of the sediments but also with the additional components (i.e., calcium sulfate) in veins (Fig. 1d). Thereby, the estimated water chemistry in the full-interaction scenario would reflect mixtures of the primary and additional components. In the no-interaction scenario, we assume that the observed secondary minerals in the matrix of the sediments are not influenced by the post-depositional $\text{SO}_4^{2-}$-rich fluids in the last wetting event (Fig. 1d). In the latter scenario, we estimate the chemical composition of the pore water using only the secondary minerals that are considered to be contained in the matrix of the sediments, i.e., akaganeite. The estimated pore water in the no-interaction scenario would reflect the primary components trapped within the sediments before the last wetting event.

**The full-interaction scenario.** We first examine the full-interaction scenario and discuss the water chemistry of the pore water at the last re-wetting event immediately before the disappearance of liquid water (Fig. 1d). The obtained X-ray diffraction (XRD) patterns of smectite\textsuperscript{12,13,21} provide information about exchangeable cations in the interlayer (Fig. 2). Basal spacing of smectite depends on the cationic composition in the interlayer and the relative humidity (RH). The cationic composition of smectite of John Klein and Cumberland are estimated from the peak deconvolutions based on the previous experimental studies of smectite basal spacing by RH controlled XRD analyses (see Method). In addition to smectite, the presence of calcium sulfate and akaganeite\textsuperscript{12,14,16} constrain the composition of liquid water.

Table 1 and Supplementary Fig. 2 show the compositions of the pore water that last interacted with the Yellowknife Bay sediments for the full-interaction scenario. The concentrations of all components from the Cumberland site overlap those from the John Klein site (Supplementary Fig. 2). This suggests that the pore-water compositions at the two adjacent sites would have been similar and may define the pore water chemistry throughout the Yellowknife Bay sediments. This is consistent with a view of the full-interaction scenario that the post-depositional fluids infiltrated into the sediments. The reconstructed similar compositions of pore water at these sites do not contradict with the fact that the top of the peaks of the 001 reflection of John Klein and Cumberland are different (Fig. 2). The peak deconvolution analyses show that the contribution of the predominant cations (Na$^+$ for John Klein and Mg$^{2+}$ for Cumberland) to the total interlayer cations are almost half (i.e., ~0.5) (Supplementary Table 1). This suggests that both of the smectites from John Klein and Cumberland are close to transition of the predominant cations in the interlayer sites, whereas that of Marimba2 is dominated by Na$^+$. In a solution within a range of compositions, a transition of the predominant cation occurs in smectite\textsuperscript{22}. Within this range of solution composition, smectites with different of cation occupancies can co-exist. Since the pore-water composition from the Cumberland site is more constrained than those from John Klein site, the former would be the representative water chemistry of the pore water prevailing in the Yellowknife Bay sediment.

There are two possible ways for the liquid pore water to have disappeared from the sediments after the final wetting event (Fig. 1d, e). The first is drying out of the liquid pore water due to complete evaporation in a warm hyperarid climate above freezing temperature. According to this, concentrations of dissolved components should increase upon drying and finally reach saturation levels of high-solubility salts\textsuperscript{23}, such as halite. The estimated concentrations of Na$^+$ correspond to weakly-to-moderately saline (hyposaline) (0.1 mol/kg) and are far below the saturation level of halite (e.g., 10 mol/kg at ambient temperature). This suggests that the scenario for the complete evaporation in warm climate can be ruled out. The other is freezing of the liquid pore water and subsequent sublimation of ground ice in a cold climate. In this case, concentrations of salinity in remained liquid water would have also occurred upon freezing. However, freezing of pore water most likely initiates at the interfaces with solid particles\textsuperscript{24}. This suggests that upon
freezing, highly concentrated brine would be unable to directly interact with smectite particles. Hence, the pore-water chemistry recorded in the Yellowknife Bay sediments most likely represents saturated pore water immediately before freezing in the last wetting event.

The dissolved components in Table 1 originate from both the primary components from the pore water in the bottom sediment of the early lake and the additional components from post-depositional fluids in the rewetting events. We believe that the predominant dissolved components of Na and Cl in the pore water would have largely originated from the primary component; namely, lake water trapped within the sediments (Fig. 1a, b). This is because both Na⁺ and Cl⁻ behave as conservative species which are generally retained in subsequent chemical reactions (e.g., diagenesis), resulting in preservation of information about bottom water within co-buried smectite on Earth. Additionally, the post-depositional SO₄²⁻–rich fluids in the last wetting event were depleted in Na. Na contents are almost zero (<0.05 wt%) at sulfate-rich veins with the highest SO₄²⁻ contents. No enrichments of Na in sulfate-rich veins in the Murray and Stimson formations may also support depletion of Na in post-depositional SO₄²⁻–rich fluids, if the fluids are in common with Yellowknife Bay.

Groundwater within terrestrial basalts typically contains low Na concentrations (10⁻⁴–10⁻³ mol/kg; see Methods). Given the possibility that the primary components could have been leached due to upwelling groundwater into Gale, the estimated Na concentration would be a lower limit of the primary Na concentration in the bottom water of the early lakes. Nevertheless, we consider that the original Na concentration in the bottom water would not be remarkably higher than those in Table 1 because of lack of evidence for drying hypersaline lakes (e.g., desiccation cracks and rip-up chips) at Yellowknife Bay. We consider that if the early lakes existed, its Na⁺ concentration would have been on the same order of magnitude as that of the pore water in the last wetting event.

Our results of the pore-water chemistry suggest that the water chemistry of the early Gale lakes would be characterized as hyposaline, at least, at the time of the Yellowknife Bay sediments deposition. The estimated Na–Cl concentrations are lower than terrestrial seawater ([Na] = 0.49 mol/kg and [Cl] = 0.56 mol/kg), but significantly higher than freshwater. On Earth, hyposaline lakes are abundant in semi-arid climate regions, such as inner-continent steppe areas. Desiccation cracks and rip-up chips are not pervasive around terrestrial hyposaline lakes (see Supplementary Fig. 3). Thus, the absence of desiccation cracks at Yellowknife Bay is compatible with our conclusion of hyposaline early Gale lakes.

Most of the terrestrial hyposaline lakes in continental areas are terminal lakes without any outflowing rivers. Lake levels of terminal lakes are maintained by a balance between inflowing water and evaporation. Through their hydrological cycles, solutes accumulate within the lakes. Our conclusion of hyposaline water suggests that the outflow of water from the Gale lakes was restricted, which is consistent with the geomorphic interpretation of the Gale lakes as potentially being closed-basin. Additionally, formation of trioctahedral smectite, including saponite, usually occurs in terrestrial alkaline-saline lakes as an alteration product by early diagenesis (Supplementary Table 2). Thus, the abundance of saponite in the Yellowknife Bay sediments is also supportive of hyposaline conditions for Gale lake water, although saponite formation may also occur through closed-system alterations of mafic minerals. Furthermore, akaganeite, a chloride-bearing ferric oxyhydroxide, occurs with smectite in the Yellowknife Bay mudstone. The formation of akaganeite requires >0.05 mol/kg of dissolved Cl concentrations in the solution. Accordingly, the Cl concentrations (0.1–0.3 mol/kg from the Cumberland site) estimated by the present study are consistent with the formation conditions of akaganeite, although the akaganeite is most likely to have been formed during the rewetting events using primary Cl in the sediments in the full-interaction scenario (see below).

We constrain the pH of the pore water based on the stability relationship of pH-sensitive secondary minerals found in the sediments. Calcium carbonates are ubiquitous in terrestrial surface conditions and frequently observed in terrestrial lacustrine sediments regardless of their origins (authigenic or clastic). However, calcium carbonates are very low (<0.8 wt%) in the Yellowknife Bay sediments. The estimated Ca concentrations in the pore water are 0.02–0.05 mol/kg from the Cumberland site (Table 1), which are high enough to produce calcium carbonates if sufficient amounts of CO₃²⁻ are available. The absence of calcium carbonates must be ascribed to limitation of CO₃²⁻ in the pore water in the last wetting event, indicating that the pore water may also be characterized by low pH and/or low levels of dissolved ΣCO₂ ([CO₂] + [HCO₃⁻] + [CO₃²⁻]), where [i] denotes concentration of the ith species in molal units. Gypsum, proposed as a late diageneric product, is thought to have been ubiquitously present throughout the entire Yellowknife Bay sediments instead of calcium carbonates. We believe that gypsum was the solubility-controlled phase of Ca at the time of the late diagenesis (see Methods). This means that

| Table 1 Estimated solution compositions of pore water that finally interacted with sediments at John Klein and Cumberland for (a) full-interaction scenario and (b) no-interaction scenario |
| --- |
| **Full-interaction scenario** | **No-interaction scenario** |
| **John Klein** | **Cumberland** | **John Klein** | **Cumberland** |
| Na (mol/kg) | 0.085±0.24 | 0.094±0.12 | 0.038±0.42 | 0.033±0.13 |
| K (mol/kg) | 0.0025±0.018 | 0.0014–0.0044 | 0.0011–0.030 | 0.00047–0.0044 |
| Mg (mol/kg) | 0.0046±0.11 | 0.035±0.060 | 0.00064–0.21 | 0.0034–0.065 |
| Ca (mol/kg) | 0.022±0.12 | 0.024–0.045 | 0.019±0.13 | 0.05–0.34 |
| Cl (mol/kg) | 0.072±0.59 | 0.11±0.25 | N/A | N/A |
| SO₄ (mol/kg) | 0.025±0.14 | 0.44±0.072 | N/A | N/A |
| ΣSO₄ (mol/kg) | 0.0019–0.041 | 0.0023–0.016 | 0.00044–0.19 | 0.00011–0.013 |
| pH | 6.7–7.3 | 6.9–7.3 | 6.5–8.3 | 6.8–8.1 |
| PCO₂ (mbar) | 6–130 | 6–40 | N/A | N/A |

The temperature is assumed to be 0 °C. Na, K, Mg, Ca, Cl, SO₄, Cl, ΣCO₂, Fe represent the total dissolved components of sodium, potassium, magnesium, calcium, chlorine, sulfate, dissolved inorganic carbon and iron, respectively.
gypsum is more stable than calcium carbonates in the water-sediment system. The stability condition between gypsum and calcium carbonates can be calculated as functions of pH and dissolved $\Sigma$CO$_2$ levels (Fig. 3).

Figure 3 shows that, unless dissolved $\Sigma$CO$_2$ levels are extremely low, an alkaline pH can be ruled out for the pore water in the last wetting event (Fig. 1d). The estimated dissolved $\Sigma$CO$_2$ in the pore water would be a mixture of both a supply of CO$_2$ from the primary components (e.g., dissolution of carbonate) and CO$_2$ dissolved in the post-depositional fluids. Thus, an assumption of no CO$_2$ supply from the primary components (e.g., absence of carbonate) provides an upper limit of the pore water’s pH. Given the present level of partial pressure of atmospheric CO$_2$ ($P_{CO_2}$) on Mars as a conservative lower limit of ancient $P_{CO_2}$ levels and dissolution equilibrium between the atmosphere and post-depositional fluids, the pore water’s pH would have an upper limit of ~7.3.

Another constraint on the pore-water pH relates to smectite. The Yellowknife Bay sediments contain ~20 wt% smectite. The detailed mineralogical investigations suggest that the smectite is composed mainly of ferrian (Fe$^{3+}$) saponite. Since Fe$^{3+}$ saponite generally forms through oxidative alterations of ferrous (Fe$^{2+}$) saponite, formation and deposition of Fe$^{3+}$ saponite through oxidative weathering of basaltic rocks are unlikely. Fe$^{3+}$ saponite needs to have been originally Fe$^{3+}$ saponite in the sediments, whichever it is of diagenesis or detrital origin. In this case, a concentration of Fe$^{2+}$ in the pore water in the last wetting event is likely to have been controlled by Fe$^{2+}$ saponite because it would be the predominant Fe$^{2+}$-bearing secondary mineral in the sediments, and because low water-rock ratios are expected in the water-sediment system. Fe$^{2+}$ concentrations in the pore water must be low to keep the observed layer spacing and compositions (see Methods). Since more Fe$^{2+}$ are provided from Fe$^{2+}$-bearing saponite at lower pH, the observed interlayer composition provides a lower limit of the pore water’s pH at ~6.9. Together with the constraint from a carbonate-gypsum stability line, we propose a circumneutral pH for the pore water in the last wetting event (Fig. 1d).

The proposed neutral pH agrees with the iron-bearing secondary mineral assemblages found by Curiosity. The Yellowknife Bay sediments possess a wide variety of secondary iron-bearing minerals (akaganeite, magnetite, and Fe$^{2+}$ saponite). Although magnetite and saponite might be of detrital origins, their relatively-high abundance suggests that the pore-water pH would be compatible with their thermochemical stability. Our quantitative reconstruction of water chemistry in the pore water enables us to construct the stability relationship of these iron minerals in regard to pH and Eh (Fig. 4). The fact that all of the observed secondary iron-bearing minerals appear in the pH range of 6.8–8.0 (Fig. 4a) strongly supports our conclusion of circumneutral pH.

In contrast to a narrow range of pH constraints, the Eh covering these secondary minerals ranges widely from upper to lower limits for the presence of liquid water at circumneutral pH (Fig. 4a). To form akaganeite in particular, high-Eh oxidants should have existed in the water-sediment system (Eh > 0.3 V at pH 7; Fig. 4a). On Mars, potential oxidants capable of producing sufficient Eh include molecular oxygen, ozone, perchloric acid, and nitric acid. Given that all of these potential candidates are proposed to form via atmospheric processes, we theorize that oxidants were transported from the surface, plausibly together with protons (i.e., H$_2$SO$_4$), so that the fluids can contain the

---

**Fig. 3** Constrained pH-$\Sigma$CO$_2$ conditions (white area) in the pore water for mean water composition of the full-interaction scenario (Cumberland). The red line shows the stability boundary between carbonate and gypsum. The orange and sky-blue areas correspond to aragonite stable conditions and saponite unstable conditions, respectively. The broken lines show $\Sigma$CO$_2$ concentrations for $P_{CO_2}$ assuming dissolution equilibrium. See Methods for calculation methodology.

**Fig. 4** Eh-pH diagram of relevant iron species for the pore-water composition of the full-interaction scenario (a) and the no-interaction scenario (b) at 0 °C and 1 atm assuming equilibrium with albite and amorphous silica. The mean water composition at Cumberland are used for the full-interaction scenario, whereas the upper limits of the concentrations are used for the no-interaction scenario.
photochemically produced oxidants and volcanic acid fog may have become trapped in surface ice/frost at Gale and subsequently melted. Fluids with oxidants would have been transported to the Yellowknife Bay sediments through cracks and then diffused into surrounding pores (Fig. 1d). Persistence of the disequilibria in the mineral assemblages strongly suggests that redox reactions in the pore water were very slow because of low temperatures and proceeded only partially due to the relatively short existence time of fluids until freezing, limited amounts of trapped oxidants, and/or high activation energy of Fe$^{2+}$ oxidation. Although acidic-oxidizing alterations would have been widespread on Hesperian Mars, their durations and temperature conditions are poorly constrained. Our results of persistence of redox disequilibria suggest that acidic-oxidizing episodes of alteration would have occurred at low temperatures and were relatively short-lived at Gale.

The no-interaction scenario. We next consider the no-interaction scenario. In the no-interaction scenario, we consider that SO$_4^{2-}$-rich fluids did not chemically interact with the matrix of the sediments (see above). In this case, the composition of pore water that finally interacted with the matrix reflects that in the early post-depositional stages immediately before the disappearance of liquid water (Fig. 1b). In the no-interaction scenario, we did not use dissolution equilibrium of calcium sulfate but used the presence of akaganeite in the matrix in addition to the exchangeable cations in the interlayer of the smectite (see Methods). In the no-interaction scenario, akaganeite needs to be formed before intrusion of SO$_4^{2-}$-rich fluids given their occurrence in the matrix of the sediments. The lower limit of pH are estimated from both the stability of Fe$^{2+}$ saponite; the same as in the full-interaction scenario. The upper limit of pH is estimated from the conditions that allow the formation of akaganeite in the matrix of the sediments (see Methods).

Table 1 and Supplementary Fig. 2 shows the water chemistry for the no-interaction scenario. The concentrations of Na and Cl are broadly close to those for the full-interaction scenario. Since the estimated Na concentrations are also significantly lower than the solubility of halite, the liquid pore water must likely disappeared via freezing and subsequent sublimation (see above). The lowest salinity of the pore water in the estimated range is 2300 mg/kg, which can still be classified as hypersaline. Our results of Na–Cl-type hypersaline water for the early Gale lakes in both the full- and no-interaction scenarios suggest that this conclusion is robust.

The pH is estimated to be 6.8–8.3. The obtained pH range is consistent with that of the full-interaction scenario. The stability fields of akaganeite and Fe$^{2+}$ saponite in regard to pH and Eh further provide constraints on the redox conditions of the pore water for the no-interaction scenario (Fig. 4b). Figure 4b shows that akaganeite is stable under low-to-neutral pH (<8) and highly oxidizing (Eh > 0.3 V) conditions (Fig. 4b). The pH-Eh conditions are consistent with the experimental investigations of the formation conditions of akaganeite. The required high Eh (>0.3 V) infers an abundance of strong oxidants in the lake water in the no-interaction scenario. On the other hand, reducing Fe$^{2+}$ saponite are also suggested to exist in the matrix of the Yellowknife Bay sediments. In the no-interaction scenario, the observed redox disequilibria (i.e., co-existence of akaganeite, magnetite, and Fe$^{2+}$ saponite) need to be formed other than intrusion of SO$_4^{2-}$-rich fluids.

One possibility to generate the redox disequilibria in the no-interaction scenario is interactions of upwelling groundwater at Gale with initially oxidized sediments after deposition. Groundwater within Martian crust would become reducing and alkaline. If reducing groundwater upwelled into oxidized sediments at Gale, Fe$^{2+}$ saponite would have formed through reduction of oxidized smectite, e.g., nontronite, by groundwater. Akaganeite in the sediments could have been also reduced into magnetite by groundwater; however, this conversion might have proceeded only incompletely due to kinetics. The occurrence of the redox disequilibria due to groundwater upwelling would be also applicable to the full-interaction scenario.

The full-interaction scenario vs the no-interaction scenario. Although we cannot conclude whether post-depositional SO$_4^{2-}$-rich fluids interacted with the matrix of the Yellowknife Bay sediments, we prefer the full-interaction scenario over the no-interaction scenario for the following reasons. First, the results of detailed analyses of Curiosity’s data show that even the Yellowknife Bay mudstones without visual calcium sulfate veins may contain small amounts of CaSO$_4$ (1.4 ± 1.4 wt.% of SO$_3$). Although this calcium sulfate in the matrix could have been of diageneric origin, this suggests that SO$_4^{2-}$-rich fluids would have diffused into the matrix of the mudstone in the last wetting event. Additionally, post-depositional fluids could seep into the matrix of the mudstones if the rewetting event persisted for >1–10$^2$ years (see above). The rewetting with this timescale could have been achieved by hydrological activity that formed small gullies and deltas at Gale after the formation of Aeolis Mons. Finally, because of the similar elemental compositions between the altered and unaltered mudstones, the early diagenesis could have occurred under isochemical conditions. Under the isochemical conditions, the simultaneous formation of the authigenic minerals with different stability fields is unlikely.

Below, we discuss the implications of the estimated water chemistry for climate and redox interactions on early Mars, as well as a possible trigger for the last wetting event. Early climate and redox interactions are discussed based on the estimated salinity of the early lakes. Given the similar values of salinity, the former discussion is applicable to both the full- and no-interaction scenarios. In contrast, we can only constrain the water chemistry of post-depositional fluids for the full-interaction scenario; accordingly, the latter discussion is only for the case in which the fluids fully interacted with the mudstone.

Implications for early Martian climate and redox states. Water chemistry revealed by the present study provides constraints on the palaeoclimate and palaeohydrology at the time when early major lake systems were active. Although the Gale impact occurred at around the Noachian/Hesperian boundary, the timing and duration of the early lakes are poorly constrained. The estimated Na concentrations of the early lakes allow us to estimate a total duration of hydrological activity at Gale until the time of the Yellowknife Bay sediments’ deposition. For both of the full- and no-interaction scenarios, the Na concentration of the early lakes is estimated to be ~0.03–0.2 mol/kg (Table 1) from Cumberland site. Combined with the proposed lake volume, a total amount of Na in the lake is obtained when the Yellowknife Bay sediments were deposited (see Methods). A total duration of hydrological activity can be estimated by division of the total amount of Na in the lake by a Na influx into the lake. Thus, short-term intermittency of lakes without removal of Na as halite burial does not reset the total duration. Assuming a steady-state lake level, the Na influx is equivalent to the product of Na concentrations in groundwater and an evaporation (or sublimation if lake surface was frozen) rate of lake water (see Methods). Using Na concentrations in groundwater in terrestrial basalts and evaporation rates derived from three-dimensional general circulation model (GCM) results, a total duration of hydrological activity...
until the deposition of the Yellowknife Bay sediments would be $10^7-10^8$ years for the mean surface temperature near the H$_2$O freezing point (see Methods). Higher temperatures (−25°C) result in shorter durations (−10$^4$ years) due to efficient evaporation (see Methods), although higher-temperature conditions are harder to achieve climatically. This duration is broadly consistent with the duration of the lacustrine environment ($10^4-10^5$ years) estimated from the thickness of the Gale sediments and typical sediment accumulation rates on Earth. Our results also show that the early Gale lakes would have been hypersaline and closed, where evaporation dominated fluid input. Together with the occurrence of similar hypersaline lakes in terrestrial steppe area and results of hydrological modeling to make a closed-basin lake at Gale, we also suggest that the early Gale lakes developed under semiarid climatic conditions, at least, during the deposition of the Yellowknife Bay sediments, which is consistent with the low values of the chemical index of alteration for these sediments. Our results of water chemistry suggest that Gale would have experienced prolonged ($10^3-10^6$ years) episodes of warm and semiarid climates in total, although these episodes might have been intermittent. Similar to soils on present-day Mars, Na-bearing salts would have contained in soils within Gale Crater before the appearance of the lakes. In warm periods, surface runoff could have transported them to the lake, providing salinity efficiently to the lake water. With this regard, our estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. With this regard, our estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit. Assuming ~1 wt% of the salt content based on present-day soils, such an estimate of lake duration would be an upper limit.

The estimated total duration of the early Gale lakes agrees with some formation timescales proposed for valley networks and Al-rich surface clays that formed in the late Noachian to the early Hesperian, although the timing of formation of valley networks and Al-rich surface clays may not be coincident with the existence of the early lakes. Although an ancient Martian ocean might have also existed in the early Hesperian, three-dimensional GCM results show that its presence is not required to explain fluvial activity at Gale Crater. The GCM results also suggest that when the total Martian surface water inventory is high, climatic conditions at the Aeolis quadrangle are humid rather than semiarid to arid (e.g., see Fig. 9 of ref. 52), although locally semiarid climates at Gale can be achieved for some orbital and atmospheric conditions. These suggest that the early Gale lakes, valley networks, and ancient shorelines might not have formed at the same time in a single climate, but they would have formed gradually through dynamic climates of prolonged warming on a cold early Mars.

Given the difficulty of sufficient warming on early Mars solely by CO$_2$-H$_2$O greenhouse gases, the total duration for warm episodes may reflect residence times of additional greenhouse gases (e.g., H$_2$ and CH$_4$) in the atmosphere, repeated periods of high solar insolation at snowy low-latitude highlands upon obliquity cycles, or combinations of both. Although outgassing H$_2$/CH$_4$ flux is uncertain, once released, CO$_2$-H$_2$CH$_4$ greenhouse gases would persist longer than 10$^3$ years against the diffusion-limited escape and photodissociation. In a manner similar to acidic-oxidizing alterations at Gale in later stages for the full-interaction scenario, we can infer that oxidants, e.g., perchlorate, chloride, ozone, and nitrate, might have also accumulated in surface ice/frost or upstream soils during a cold period in the early Hesperian prior to warming, which in turn could have been released into aqueous environments upon warming, e.g., triggered by H$_2$/CH$_4$ outgassing. The released oxidants might have been consumed via reactions with abundant reductants from rock components during prolonged warm episodes in the early Hesperian; whereas redox disequilibria would have been preserved due to short-term warming in the late Hesperian or later (see below). We propose that dynamic climates on early-Hesperian Mars might have been a thermochemical drive to promote redox interactions in aqueous environments, which could have provided free energy to drive the onset of chemical evolution on this planet.

Timing and trigger for acidic-oxidizing alterations. We then turn to a climatic trigger for the last warming event at Gale that caused post-depositional, acidic-oxidizing alterations after sedimentation of the Yellowknife Bay mudstone in the full-interaction scenario. Our results of low levels of dissolved CO$_2$ in the pore water (Table 1) require both low CO$_2$ supply from the primary components and low dissolved CO$_2$ in the post-depositional fluids (see above). The former suggests the absence of carbonate in the matrix of the sediments. Given that post-depositional fluids would have originated from the surface in the full-interaction scenario, the latter may reflect low P$_{CO_2}$ at the time of the last wetting event at Gale. Alternatively, dissolution equilibrium between post-depositional SO$_2^{2−}$/rich fluids with atmospheric CO$_2$ was not achieved (e.g., due to rapid melting of ice). Drawdown of CO$_2$ from fluids during transportation to Yellowknife Bay via carbonate formation is unlikely given the acidity of fluids. Based on a lower limit of pH, we propose an upper limit of P$_{CO_2}$ of ~100 mbar if atmospheric CO$_2$ was in equilibrium with the fluids (Table 1). Although formation of Fe carbonate can be kinetically inhibited even at high CO$_2$ levels, a previous bottom-up approach to estimate dissolved CO$_2$ provided an upper limit of P$_{CO_2}$ levels as tens of mbar. The consistency between these independent approaches shows robustness of low CO$_2$ in the pore water. We consider that the estimated P$_{CO_2}$ would reflect a recent atmosphere at the time of the last wetting event at Gale. The estimated P$_{CO_2}$ suggests that the last wetting event may have occurred in the late Hesperian or even the Amazonian, when atmospheric pressure would have already declined closer to the present-day level. The estimated timing of this last wetting event is consistent with the youthful age of jarosite in the Mojave2 sample (2.12 ± 0.36 Ga), drilled from a lacustrine mudstone ~60 m higher in the stratigraphic section than the Yellowknife Bay sediments. The last wetting event might be caused by a relatively short warming pulse from the obliquity variations $\omega$ would last 1–10$^3$ years, rather than episodic warming due to the release of CH$_4$ by clathrate destabilization into a dense CO$_2$ atmosphere.

Methods

Mineralogical constraints on water chemistry. We estimate water chemistry of pure water based on the following constraints from the samples at the Cumberland and John Klein drilling sites: (a) the basal spacing of smectite, (b) the presence of saponite, (c) the mineral composition of sulfate, and (d) the presence of akaganite.

The interlayer cationic compositions of smectites were estimated from the 001 reflections. The peak intensities of the 001 reflections are related to the abundance of the cationic components in the interlayer, the atomic structure factors of each component, and the Lorentz-polarization (LP) factors. The peak deconvolutions of the 001 reflections of John Klein and Cumberland sites after LP factor and the background corrections were conducted using the Pseudo-Voigt function to estimate the cation compositions (Supplementary Fig. 4). The combinations of the three peaks at 13.7, 11.5–11.7, and 10.0–10.1 Å can reasonably reproduce the 001 reflections for both smectites.

The basal spacing of smectite depends on a cation composition in the interlayer and RH. The RH remains <1% inside CheMin under temperatures 5–25°C (ref. 13). Supplementary Fig. 5 summarizes the basal spacings of several smectites with different cations (Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$) at RH = 50%. The basal spacings of Na$^+$ and K$^+$ smectites are ~10 Å; whereas, those of Ca$^{2+}$ smectite are...
scattered, but most of the smectites exhibit peaks at ~12 Å. The basal spacing of Fe²⁺ and Fe³⁺ smectite at RH = 0% (ranging 11–12.5 Å) are similar to that of Ca²⁺ smectite. The 0.6 mg smectite varied from 13–13.5 Å and these spacings are generally higher than those of Ca smectite because the hydration states of Mg²⁺ in smectite are kept even at low relative humidity. According to the relationship, the peak with 10.0–10.1 Å from the two smectites represent the Na⁺ and/or K⁺. That with 12.Å represent Mg²⁺, Fe²⁺ (Fe³⁺ and/or Fe⁴⁺), and that with 13.7 Å most likely represents the Mg²⁺. Partially intercalated hydroxylated Mg (i.e., MgOH⁺) in the interlayer site of the smectite at Cumberlind has been proposed as an explanation for the expanded structure. The dissolved MgOH⁺ species into the interlayer occurs very inefficiently at ambient to low temperatures. However, concentration of ΣMg²⁺ (eq. MgOH⁺) also becomes extremely low at high pH (pH > 10) because of the formation of Mg-bearing secondary minerals (saponite and brucite). Therefore, the low [MgOH⁺] at alkaline pH, the exchange of the dissolved MgOH⁺ species into the interlayer occurs very inefficiently at ambient to low temperatures unless the Mg²⁺/(Na⁺ - K⁺) ratio in the pore water is extremely high. Assuming the peak from 10 Å represents Na⁺ and/or K⁺, the extremely high Mg²⁺/(Na⁺ + K⁺) ratio contradicts with Na⁺/K⁺ interlayers. Although the reported basal spacings of Mg-saturated saponite vary from 11.5 to 12.0 Å, we believe that Mg²⁺-saturated Mg smectite is responsible for the spacing of ~14 Å of the smectites. This is the case because the swelling behaviors of interlayer cations mainly depend on the layer charge and charge location. Vermiculite is a high-layer charge montmorillonite, and well-crystallized hydroxylated Mg (i.e., MgOH⁺) becomes important only at extremely low or high pH. The major cations in the solutions must be very low due to formation of Mg/Ca-bearing secondary minerals. Consequently, the low concentrations of divalent cations lead to the precipitation equilibrium of gypsum. The dissolved Fe³⁺ has been observed in the Yellowknife Bay sediments95. Although the concentrations of total chloride ([Cl⁻ + (ClO₄⁻)]) and that of cations in solutions, pH, and salinity of the pore water do not change even when the pore water contained ClO₄⁻. However, the presence of the Ca²⁺-bearing akaganeite in the Yellowknife Bay sediments suggests the concentration of Cl⁻ must be higher that than ClO₄⁻ ([ClO₄⁻]).

The cation compositions in the interlayers of smectite were calculated using the cation exchange equilibria as follows:

\[ X : Na⁺ + K⁺ = X: K⁺ + Na⁺ \]

The interlayer compositions of smectites observed from the sediments is considered to be Fe²⁺ saponite, which would have been formed by the alteration of Fe³⁺ saponite. Since the oxidation of Fe²⁺ to Fe³⁺ should have decreased the layer charge by substitution of O²⁻ for OH⁻, the smectite in the Yellowknife Bay sediments would have lower layer charge. By using the peak deconvolutions of 001 reflections, the cationic composition of smectites are determined. The concentration of dissolved ferric iron is extremely low except for the extremely low or high pH conditions. The direct intercalation of Fe³⁺ species into the interlayer site of the smectite at Cumberlind has been proposed as an explanation for the expanded structure. The dissolved MgOH⁺ species into the interlayer occurs very inefficiently at ambient to low temperatures. However, concentration of ΣMg²⁺ (eq. MgOH⁺) also becomes extremely low at high pH (pH > 10) because of the formation of Mg-bearing secondary minerals (saponite and brucite). Therefore, the low [MgOH⁺] at alkaline pH, the exchange of the dissolved MgOH⁺ species into the interlayer occurs very inefficiently at ambient to low temperatures unless the Mg²⁺/(Na⁺ - K⁺) ratio in the pore water is extremely high. Assuming the peak from 10 Å represents Na⁺ and/or K⁺, the extremely high Mg²⁺/(Na⁺ + K⁺) ratio contradicts with Na⁺/K⁺ interlayers. Although the reported basal spacings of Mg-saturated saponite vary from 11.5 to 12.0 Å, we believe that Mg²⁺-saturated Mg smectite is responsible for the spacing of ~14 Å of the smectites. This is the case because the swelling behaviors of interlayer cations mainly depend on the layer charge and charge location. Vermiculite is a high-layer charge montmorillonite, and well-crystallized hydroxylated Mg (i.e., MgOH⁺) becomes important only at extremely low or high pH. The major cations in the solutions must be very low due to formation of Mg/Ca-bearing secondary minerals. Consequently, the low concentrations of divalent cations lead to the precipitation equilibrium of gypsum. The dissolved Fe³⁺ has been observed in the Yellowknife Bay sediments. Although the concentrations of total chloride ([Cl⁻ + (ClO₄⁻)]) and that of cations in solutions, pH, and salinity of the pore water do not change even when the pore water contained ClO₄⁻. However, the presence of the Ca²⁺-bearing akaganeite in the Yellowknife Bay sediments suggests the concentration of Cl⁻ must be higher that than ClO₄⁻ ([ClO₄⁻]).

The charge balance of the solution can be expressed as:

\[ \{Na⁺\} + (K⁺)^+ + 2\{Mg²⁺\} + 2\{Ca²⁺\} + 2\{Fe³⁺\} = [Cl⁻]^+ + 2\{SO₄²⁻\}. \]

Although we consider aqueous complexes in the calculation, the charge balance expressions in the manuscript ignore the aqueous complexes for illustrative purpose. (Ca²⁺) and (SO₄²⁻) are constrained from dissolution equilibrium of gypsum (see above) for full-interaction scenario:

\[ CaSO₄ \cdot 2H₂O = Ca²⁺ + SO₄²⁻ + 2H₂O. \]

The corresponding mass action expression is expressed as follows:

\[ K_c = a_{Ca²⁺} a_{SO₄²⁻} = 236 \times 10⁻⁶ [CaSO₄ \cdot 2H₂O]. \]

where, γ represents the activity coefficients of rith species. Based on the constrain from the water type of NaCl, the equivalent concentrations of Na⁺ and Cl⁻ are higher than the major species such as Mg²⁺, Ca²⁺ and SO₄²⁻. Therefore, the endmember compositions of solutions at an interlayer cationic composition under a single set of selectivity coefficients can be determined following two boundary conditions:

\[ \{Na⁺\} = 2\{Di²⁺\}, \]

(7)

\[ Cl⁻ = 2\{SO₄²⁻\}. \]

(8)

where [Di²⁺] represents the concentrations of divalent cations, of which concentrations are higher next to that of Na⁺. We calculated the two endmember solution compositions from Eqs. (7) and (8) under the ranges of the selectivity coefficients with the uncertainties.
In the no-interaction scenario, the matrix of the mudstone is assumed to be isolated from post-depositional fluids enriched in sulfate. Therefore, the charge balance of the solution can be expressed as:

\[
(Na^+) + (K^+) + 2(Fe^{2+}) + 2(Ca^{2+}) + 2(Fe^{3+}) = (Cl^-).
\]

The constraint on \([Cl^-]\) with regard to the existence of akaganeite in the mudstone is applied to the no-interaction scenario (i.e., \([Cl^-] \geq 0.05 \text{mol/kg}\)) instead of the constrain from Eq. (8).

**Constraining pH and dissolved \(CO_2\) in the full-interaction scenario.** The formation of calcite, most stable calcium carbonate phase, is known to be kinetically inhibited in the presence of significant amount of \(Mg^2+\) in solutions7. Instead, metastable aragonite is favored to form from the solutions9. The stability relationship between aragonite and gypsum is written as:

\[
\text{CaCO}_3 + \text{SO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O} = \text{CaSO}_4 + 2\text{H}_2\text{O} + \text{CO}_2(aq).
\]

The Gibbs free energy \((\Delta G_0)\) of the reaction can be written as:

\[
\Delta G_{R,10} = \Delta G_{R,10}^{0} + RT \ln \left( \frac{d_{\text{CaCO}_3} \cdot d_{\text{CaSO}_4} \cdot d_{\text{H}_2\text{O}}}{d_{\text{CO}_2(aq)}} \right)
\]

\[
\Delta G_{R}^{0}\text{represents the standard free energies of the reactions and is related to the equilibrium constants}\text{. The equilibrium constant of Eq. (10) was calculated using the RXN program in the GWB.}\]

---

**Code for all analyses will be made available on request.**

---

Received: 18 July 2018; Accepted: 1 October 2019; Published online: 25 October 2019
63. Peretyazhko, T. S. et al. Reaction of akaganeite with Mars-relevant anions. **ACS Earth Sp. Chem.** 3, 314–323 (2019).
64. Bethke, C. M. *The Geochemist’s Workbench Users Guide.* (University of Illinois, 1998).
65. Helgeson, H. C., Kirkham, D. H. & Flowers, G. C. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°. *Am. J. Sci.*** **281**, 1249–1516 (1981).
66. Kristmannsdóttir, H. & Ármannsson, H. Groundwater in the Lake Myvatn area, northern Iceland: chemistry, origin and interaction. *Aquat. Ecol.* 38, 115–128 (2004).
67. Tweed, S. O., Weaver, T. R. & Cartwright, I. Distinguishing groundwater flow paths in different fractured-rock aquifers using groundwater chemistry: Dandenong Ranges, southeast Australia. *Hydrogeol. J.* 13, 771–786 (2005).
68. Coombs, M. J. Threats to water quality in the deep basalt aquifer, city of Walla Walla, Washington. (Whitman College, 2000).
69. Martínez, G. M. et al. The modern near-surface martian climate: a review of in-situ meteorological data from viking to curiosity. *Space Sci. Rev.* 212, 295–338 (2017).
70. Brutsaert, W. *Hydrology: An introduction.* (Cambridge University Press, 2005).

**Acknowledgements**

discussions with T. Kasama, T. Sato, T. Shibuya, and S. Yokoyama are greatly appreciated. Financial support was provided by KAKENHI from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) (Grant Nos. JP17H06458, JP17H06454, and JP17H06456) and a cooperative research program of the Institute of Nature and Environmental Technology, Kanazawa University (No. 19035).

**Author contributions**

K.F., H.S. and K.M. modeled the water chemistry. Y.S. interpreted the estimated water chemistry. The estimate of the duration of the early Gale lakes was conceptualized by R.W. and Y.S., and calculated by Y.S. and R.W. All authors wrote the paper.

**Competing interests**
The authors declare no competing interests.

**Additional information**

Supplementary information is available for this paper at https://doi.org/10.1038/s41467-019-12871-6.

**Correspondence** and requests for materials should be addressed to K.F.

**Peer review information** *Nature Communications* thanks Edwin Kite, Elizabeth Rampe, Mikhail Zolotov and other anonymous reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

**Reprints and permission information** is available at [http://www.nature.com/reprints](http://www.nature.com/reprints)

**Publisher’s note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2019