Origin of acidic surface waters and the evolution of atmospheric chemistry on early Mars

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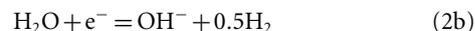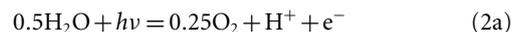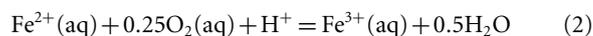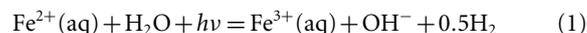
Observations from *in situ* experiments and planetary orbiters have shown that the sedimentary rocks found at Meridiani Planum, Mars were formed in the presence of acidic surface waters[1-4]. The water was thought to be brought to the surface by groundwater upwelling[5,6], and may represent the last vestiges of the widespread occurrence of liquid water on Mars. However, it is unclear why the surface waters were acidic. Here we use geochemical calculations, constrained by chemical and mineralogical data from the Mars Exploration Rover Opportunity[7-10], to show that Fe oxidation and the precipitation of oxidized iron (Fe^{3+}) minerals generate excess acid with respect to the amount of base anions available in the rocks present in outcrop. We suggest that subsurface waters of near-neutral pH and rich in Fe^{2+} were rapidly acidified as iron was oxidized on exposure to O_2 or photo-oxidized by ultraviolet radiation at the martian surface. Temporal variation in surface acidity would have been controlled by the availability of liquid water, and as such, low-pH fluids could be a natural consequence of the aridification of the martian surface. Finally, because iron oxidation at Meridiani would have generated large amounts of gaseous H_2, ultimately derived from the reduction of H_2O, we conclude that surface geochemical processes would have affected the redox state of the early martian atmosphere.

The sedimentary rocks examined by the Mars Exploration Rover Opportunity reflect an ancient climate in transition. Deposited ~3.7 billion years ago in an arid environment punctuated by episodes of groundwater upwelling, these siliciclastic-saline sediments record the last vestige of an era when liquid water was more common than at present. The sediments contain jarosite and other mineral phases diagnostic of formation from acidic (pH ~2–4), Fe-rich surface waters[11]. Meridiani data are a cornerstone for interpreting the early chemical evolution and habitability of our planetary neighbour, yet the origin of surface acidity and redox conditions at the time of deposition are largely unknown.

Outcrop microtextures, sedimentology and mineralogy[1-4], as well as geophysical–hydrological modelling[5,6], all indicate that a fluctuating groundwater table drove episodic deposition and modification of chemical sediments at Meridiani Planum and elsewhere on the late Noachian surface of Mars. The inescapable consequence of even limited interaction between subsurface groundwaters and a basalt-dominated aquifer is buffering to circum-neutral pH and anoxia, in turn allowing solubilization and transport of Fe^{2+}. However, paradoxically, Mars Exploration Rover

data indicate that Fe was almost entirely oxidized during chemical sediment formation and/or early diagenesis in a dune–interdune–playa depositional setting, pointing to an effective atmospheric oxidant. What then were the consequences of wholesale Fe oxidation occurring at the interface between emerging groundwater and the atmosphere? *In situ* measurement of Meridiani outcrop chemistry and mineralogy make it possible to quantify the amount of acid consumed or produced during Fe oxidation and Fe^{3+} mineral precipitation. The acid produced can then be titrated against the available base-anion content measured in outcrop (that is, SO_4^{2-}, Cl^-, PO_4^{3-} and CO_3^{2-}), yielding a net proton balance reflective of the parent fluid. For our titration method (fully described in the Supplementary Information), we sum the number of moles of H^+ generated during the precipitation of a measured quantity and distribution of Fe^{3+}-bearing secondary minerals, using data collected through sol 548 of the Opportunity mission on 19 Meridiani Planum outcrop targets[7-10].

Anoxic (rock-buffered) aquifer fluids rich in Fe^{2+} (derived from basalt) would have oxidized on emergence either by photo-oxidation (reaction (1)) in the presence of ultraviolet light, or by dissolved molecular O_2 (reaction equation (2)) ultimately derived from atmospheric H_2O (reactions (2a) and (2b)):

$$Fe^{2+}(aq) + H_2O + h\nu = Fe^{3+}(aq) + OH^- + 0.5H_2 \qquad (1)$$

$$Fe^{2+}(aq) + 0.25O_2(aq) + H^+ = Fe^{3+}(aq) + 0.5H_2O \qquad (2)$$

$$0.5H_2O + h\nu = 0.25O_2 + H^+ + e^- \qquad (2a)$$

$$H_2O + e^- = OH^- + 0.5H_2 \qquad (2b)$$

We assume that all dissolved Fe^{3+} would have precipitated to form schwertmannite ($FeO(OH)_{0.75}(SO_4)_{0.125}$; see justification in Supplementary Information) through precipitation from solution[12]:

$$Fe^{3+}(aq) + 0.125SO_4^{2-} + 1.75H_2O$$
$$= FeO(OH)_{0.75}(SO_4)_{0.125} + 2.75H^+ \qquad (3)$$
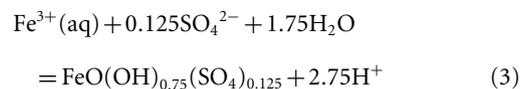
We then assume that schwertmannite dissolves and reprecipitates to form a mixture of jarosite (($K, Na)Fe_3(SO_4)_2(OH)_6$, reaction (4)) and goethite ($FeO(OH)$, reaction (5)), which ultimately

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Table 1 | Summary of titration calculations.

Mol kg^{-1} outcrop unless noted		Bylot_RAT		Ontario_London_RAT	
Total Fe		2.46		2.02	
Fe3D3 (% subspectral area)*[†]		14		19	
Haematite (% subspectral area)		41		35	
Jarosite (% subspectral area)		30		27	
H$^+$ produced		3.36		2.63	
		pH 2	pH 4	pH 2	pH 4
H$^+$ titrated	as S (VI)	0.92	1.8×10^{-2}	1.24	2.4×10^{-2}
	as Cl$^-$	4.5×10^{-3}	4.5×10^{-5}	1.1×10^{-2}	1.1×10^{-4}
	as P (V)	0.37	0.29	0.40	0.31
	as C (IV)[‡]	0.46	0.46	0.46	0.46
H$^+$ remaining		1.61	2.59	0.52	1.84

Data are presented for samples with the most (Ontario_London RAT) and least (Bylot_RAT) acid titrated relative to the amount of acid produced during oxidation and mineral precipitation. The total iron content and ferric mineral distribution allows for calculation of total acid (H$^+$) produced, which is then titrated against available bases at pH 2 and 4, leaving the indicated amount of H$^+$ remaining. See Supplementary Information for details on all 19 outcrop analyses.

*Represents the percentage of Fe atoms associated with each phase determined by the Mössbauer spectrometer. Note that the three phases do not sum to 100% because there are other primary igneous Fe^{2+}-bearing minerals present (olivine, pyroxene) that do not bear on our calculations.

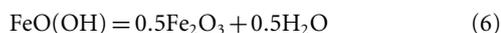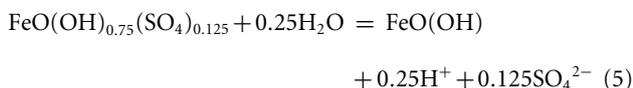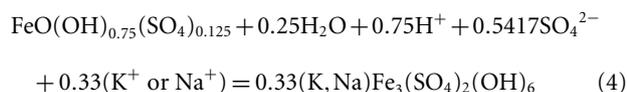[†]Fe3D3 is the name given to a nanophase component having non-unique Mössbauer spectral attributes that are consistent with one or a combination of: schwertmannite, superparamagnetic goethite or haematite, ferrihydrite and akaganeite[10]. For the purposes of our analysis, we assume Fe3D3 is schwertmannite having the formula FeO(OH)$_{0.75}$(SO$_4$)$_{0.125}$.

[‡]Calculated from an upper limit of 2.3 wt% CaCO$_3$ in outcrop[29,30].
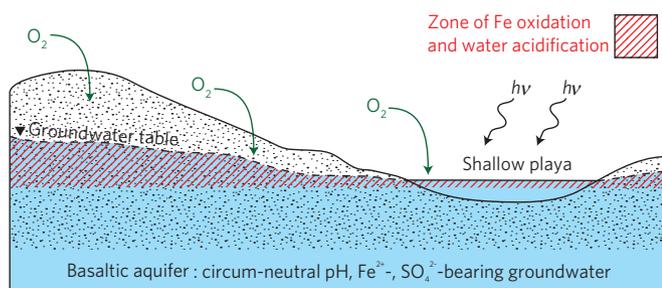
Figure 1 | Groundwater emergence at Meridiani Planum. Schematic cross-section showing the emergence of an Fe^{2+}- and SO$_4^{2-}$-bearing groundwater from a porous basaltic aquifer (stippled region). The fluid is buffered to circum-neutral pH and anoxia, and undergoes oxidation at the interface between grounwater and the atmosphere. Ferric mineral precipitation reactions, enabled by ultraviolet-promoted oxidation in surface waters (reaction (1)) and O$_2$-promoted oxidation (reaction (2)) in both the vadose zone and surface waters, generate substantial acidity in the area indicated by red hatching.

dehydroxylates to form haematite (Fe$_2$O$_3$, reaction (6)):

$$FeO(OH)_{0.75}(SO_4)_{0.125} + 0.25H_2O + 0.75H^+ + 0.5417SO_4^{2-}$$

$$+ 0.33(K^+ \text{ or } Na^+) = 0.33(K, Na)Fe_3(SO_4)_2(OH)_6 \quad (4)$$

$$FeO(OH)_{0.75}(SO_4)_{0.125} + 0.25H_2O = FeO(OH)$$

$$+ 0.25H^+ + 0.125SO_4^{2-} \quad (5)$$

$$FeO(OH) = 0.5Fe_2O_3 + 0.5H_2O \quad (6)$$

Having arrived at a value for total acid generated to form the measured concentration and distribution of schwertmannite, jarosite and haematite in outcrop through reactions (1)–(6), titration of that acid against the measured concentrations of base anions in outcrop yields the net proton balance, in acidity or basicity of each sample. The acid titrating properties of these bases are themselves a function of pH (Supplementary Fig. S1), which is constrained by the presence of jarosite at about pH 2–4.

For all 19 outcrop analyses (Table 1 and Supplementary Tables S1–S4) there is an excess of H$^+$ generated in forming the observed secondary Fe^{3+} mineral phases relative to the available titrant in outcrop. Our results are valid at standard temperature and pressure for any initial fluid pH ≤ 7 because the ratio of H$^+$/OH$^-$ in the ambient fluid is ≥ 1, and so we need not consider titration against OH$^-$. We suggest that the results are also valid for fluids with higher initial pH values if we assume approximately millimolar dissolved Fe^{2+} concentrations, in accordance with ref. 13. Our calculations imply that as long as redox conditions in the aquifer were conducive to the transport of Fe^{2+}(aq) from the subsurface, Fe oxidation and formation of schwertmannite, jarosite and haematite would have resulted in the generation of low-pH fluids at the site of Fe^{3+} mineral precipitation, as shown in Fig. 1. The acid generated would have been available to react with primary mineral phases (for example, materials analogous to the basaltic sand that covers the present-day Meridiani surface) or with deeper lithologies if acidic waters retreated into the subsurface, in a manner analogous to that suggested in refs 14,15. Note that we have considered only acid-producing reactions that are based on Fe chemistry; the oxidation of reduced sulphur species (for example, H$_2$S, SO$_2$), from which outcrop SO$_4^{2-}$ must ultimately be derived, could have produced more acid (for example, ref. 16). The critical result, however, is that iron oxidation and iron mineral precipitation are sufficient to have generated the acidity recorded by the mineral assemblage at Meridiani Planum. Accordingly, input of acid volatiles (for example, SO$_2$, H$_2$SO$_4$) at the site of sediment formation[17–19] is not required and SO$_4^{2-}$ can be considered a background constituent of the aquifer fluid (Fig. 1).

Our analysis permits an estimate of the volume of water supplied to the region to form the Meridiani Planum succession. We calculate that 95 l of H$_2$O per kg of outcrop is required to dissolve the average amount of H$^+$ remaining after titration (Supplementary Table S3) and generate a pH = 2 fluid. This value is then multiplied by the mass of Meridiani Planum outcrop (Supplementary Table S5 and Fig. S2) to derive a total water volume. We arrive at a value of 7×10^{18}–3×10^{19} l for a 200–800-m-thick deposit. This estimate is in reasonable agreement with an independent groundwater flow modelling study[5], which reports an integrated water flux to the surface equivalent to a 2.5–17 km water column, or 5×10^{17}–3×10^{18} l over the total area
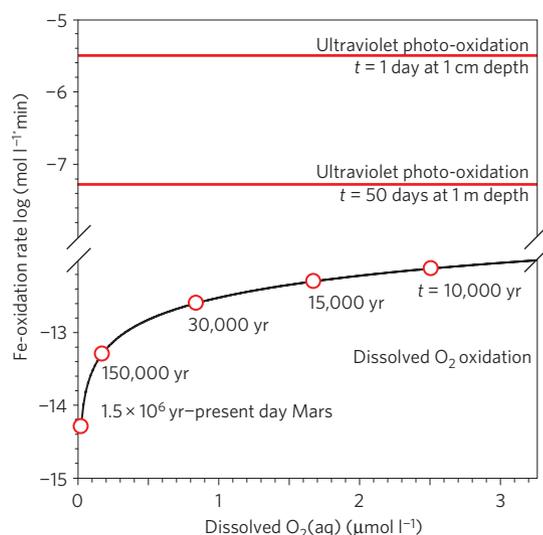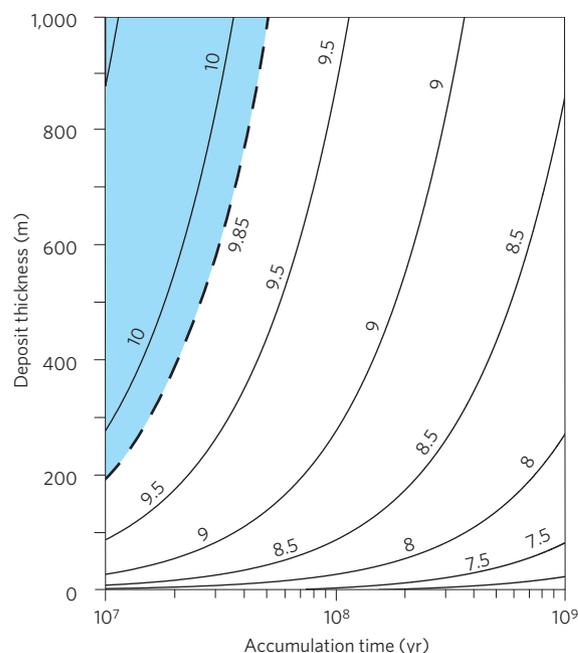
Figure 2 | Oxidation timelines at Meridiani Planum. Oxidation rates for ultraviolet- and dissolved-O_2-promoted oxidation of a 4 mM solution of Fe^{2+}(aq) at 20–25 °C and pH ≤ about 4.0. The rates of the former are plotted as a function of water depth, whereas the rates of the latter depend on $(O_2$(aq)). Also shown are the approximate times required for the complete oxidation of the 4 mM Fe^{2+}(aq) solution at the corresponding rate.

Figure 3 | Hydrogen-escape rates for Fe oxidation at Meridiani Planum. Escape rates (log mol H_2^* yr^{-1}) plotted as a function of the thickness of Meridiani Planum outcrop (m) and the time over which the entire volume of outcrop accumulates (years). The blue field indicates a solution space with a higher required H_2-escape rate than can be accounted for by the Jeans escape rate reported in ref. 23.

of Meridiani Planum. However, if we carry out the same calculation for our pH = 4 case, the required water volume estimates increase by ~2 orders of magnitude—a gross overestimate compared with results from groundwater modelling[5]. This substantial volume increase highlights the important role water has in diluting the acid produced by Fe redox processes.

Redox-driven surface acidity requires that iron oxidation was fast enough to occur in the playa-vadose zone sediment source region described in ref. 1. Figure 2 illustrates experimental rates for ultraviolet-promoted photo-oxidation[20] and oxidation by dissolved molecular O_2(aq) (ref 21; see Supplementary Information for details). Ultraviolet-promoted Fe-oxidation rates are extremely rapid, with complete oxidation occurring within ~1–50 days depending on water column depth. Under the pH range considered, the oxidation of Fe^{2+}(aq) by molecular O_2 is characteristically slow[21]. Incoming aquifer fluids, however, would have arrived at circum-neutral to alkaline pH. Accordingly, initial rates of oxidation would have been orders of magnitude faster than indicated for dissolved O_2 in Fig. 2, slowing only as acid production drove pH downwards (oxidation rates increase by a factor of 100 for every unit increase in pH above pH = 4; ref. 21). For either mechanism, available rates were sufficient to drive the rapid oxidation of Fe over geologically short timescales, and are consistent with fluid acidification during groundwater emergence (Fig. 1).

The geochemistry of sedimentary rocks at Meridiani Planum shares important connections with the redox state of the atmosphere and can therefore provide constraints on atmospheric loss processes operating during the late Noachian. For both pathways (reactions (1) and equation (2), above), the electrons lost from iron during oxidation are used to reduce protons from water to H_2. Ultimately, the generation of acidity by oxidation of Fe^{2+} in surface fluids is tied to the fate of H_2, and the primary process responsible for net surface oxidation is planetary H_2 escape[22]. From outcrop chemistry, we can calculate the rates of H_2 production, and hence the required H_2-escape rate, for oxidation and acidification at Meridiani Planum. We use our estimate of the total mass of the Meridiani Planum deposit, varied as a function of outcrop thickness, to determine the total H_2 yield for production of the Fe^{3+}

abundance measured in outcrop (average = 1.84 mol Fe^{3+} kg^{-1}, Supplementary Table S1). The details of this calculation and its sensitivity to outcrop area, density and porosity can again be found in the Supplementary Information. This amount of H_2 production is divided by a range of plausible accumulation times for the sediments at Meridiani Planum, and is plotted in Fig. 3.

A significant portion of the solution space, characterized by the rapid (10–50 Myr) accumulation of a relatively thick (200–1,000 m) deposit, indicates that H_2-escape rates required for net surface oxidation are greater than that predicted for present-day thermal (Jeans) escape processes alone[23]. We note that the use of the Jeans escape rate from ref. 23 as a benchmark assumes a constant H_2-loss rate throughout geological time. The required H_2-escape rates shown in Fig. 3, however, are fundamentally minimum estimates because they consider only the oxidation occurring at Meridiani Planum. Coeval deposits elsewhere on Mars (for example, refs 5,6) would have added significantly to the oxidation demand. Given the absence of a complementary electron-rich reservoir preserved in the ancient crust (for example, significant sulphide mineral or reduced C-bearing deposits), these results may indicate the operation of H_2-escape processes such as hydrodynamic escape[24] or non-thermal solar-wind stripping[25]. The former mechanism would imply the continued removal of a H-rich atmosphere ~3.7 Gyr ago, significantly later into martian geologic history than is generally thought[26,27], and a counterintuitive result given the evidence for widespread surface oxidation at Meridiani Planum.

Our analysis demonstrates the existence of two separated and chemically distinct aqueous environments at Meridiani Planum: a subsurface hydrosphere disconnected from the atmosphere and buffered to circum-neutral pH and anoxia by basalt–water interactions, and a surface hydrosphere driven to acidity by rapid oxidation of Fe^{2+} in the presence of potent atmospheric oxidants. Of critical importance to the pH state of this surface hydrosphere is the availability of liquid water to dilute acid produced by redox processes, and thus acidity is linked directly to aridification

of the martian surface. Observations of an apparent temporal evolution in martian surface mineralogy prompted ref. 28 to suggest a net acidification of the martian surface resulting from an increase in the rate of acid volatile supply from volcanic activity. Although this mechanism could have been important, our results indicate that redox processes were the critical driver of acidification at Meridiani Planum and potentially elsewhere on the late Noachian surface of Mars.

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Author contributions

J.A.H. carried out data analysis, modelling and wrote the paper, W.W.F. and J.A.H. conceived the study, N.J.T. and R.E.M. contributed to modelling and W.W.F., N.J.T. and R.E.M. contributed to writing.