GeoEng_Large_Aerosol and by more than 30 years for GeoEng_Small_Aerosol (Fig. 3B). Assuming a vertical expansion of the ozone hole, the first stage of recovery would be delayed by another 30 years for both cases (Fig. 3C). The recovery of Antarctic ozone to conditions that prevailed in 1980 would be delayed until the last decade of this century by geoengineering, assuming no vertical expansion of the ozone loss region (Fig. 3B). However, if the vertical extent of the ozone hole were to increase, this stage of recovery would not occur within this century (Fig. 3C).

Our estimates of the risk of geoengineering do not consider several important effects. A possible consequence of a stratospheric sulfur injection, which was not considered here, is a strengthening of the polar vortex, because of the stronger temperature gradient between high and low latitudes caused by enhanced stratospheric aerosol (*20*). This could increase the frequency of cold polar winters, leading to even greater ozone loss than estimated. On the other hand, volcanic aerosols might result in dynamic instabilities, causing earlier major stratospheric warming at the end of Arctic winters, which results in smaller PACl and therefore less ozone loss. Also, enhanced sulfate aerosols could suppress denitrification in the polar vortices in a manner that might affect the linear relation between ozone loss and PACl. Enhanced ozone loss through geoengineering would also likely result in a thinning of the ozone layer at mid-latitudes due to the export of polar processed air, as observed during the period of rising halogen loading (1979 to 1995) (*21*). Further, the enhanced stratospheric aerosol levels would disturb ozone photochemistry in mid-latitudes, resulting from the suppression of stratospheric NO_x, leading to even further ozone depletion (*22*). Additional uncertainty results from our use of idealized aerosol size and perturbation. Finally, the impact on ozone of any future major volcanic eruption would likely exceed, by large amounts, the ozone loss that was observed after the eruption of Mount Pinatubo and El Chichón, because additional volcanic aerosols will be acting on an already perturbed stratospheric SAD layer. Comprehensive chemistry–climate model simulations, considering these effects and perhaps others, are needed to fully evaluate the impact of geoengineering on atmospheric ozone.

A substantial increase of stratospheric sulfate aerosol densities caused by various geoengineering approaches will likely result in strongly enhanced chemical loss of polar ozone during the next several decades, especially in the Arctic. The expected recovery of the Antarctic ozone hole due to a reduction in stratospheric halogen loading, brought about by the implementation of the Montreal Protocol, could be delayed by between 30 and 70 years by the aerosol perturbation associated with geoengineering.

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23. We acknowledge K. Drdla for helpful discussions and for sharing her formula to calculate T_{ACl} and PACl (*14*), P. Rasch for a very helpful discussion about the SAD distributions, and the UK Meteorological Office for providing meteorological analyses. The University Corporation for Atmospheric Research (UCAR) supported the portion of this work conducted at NCAR and the NASA Atmospheric Composition, Modeling, and Analysis Program supported the portion of this work conducted at the University of Maryland.

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Water Activity and the Challenge for Life on Early Mars

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In situ and orbital exploration of the martian surface has shown that acidic, saline liquid water was intermittently available on ancient Mars. The habitability of these waters depends critically on water activity (a_{H_2O}), a thermodynamic measure of salinity, which, for terrestrial organisms, has sharply defined limits. Using constraints on fluid chemistry and saline mineralogy based on martian data, we calculated the maximum a_{H_2O} for Meridiani Planum and other environments where salts precipitated from martian brines. Our calculations indicate that the salinity of well-documented surface waters often exceeded levels tolerated by known terrestrial organisms.

Because liquid water is required by all organisms on Earth, evidence of current or past water has been viewed as a first-pass filter for habitable environments on Mars. Further evaluation of habitability, however, requires that we move beyond the mere presence of water to consider its properties. Water may be required for life on Earth, but not all terrestrial waters are habitable; the limits of terrestrial life are defined by additional parameters, including temperature, pH, and salinity (*1*).

Layered martian rocks exposed on the Meridiani plain have been interpreted as sandstones containing Mg sulfate, Ca sulfate, jarosite [(K, Na, H_3O)($Fe_{3-x}Al_x$)(SO_4)$_2$(OH)$_6$, where $x < 1$], and hematite (*2*–*5*). The geochemical, textural, and sedimentological features of these rocks are consistent with deposition in an arid, predominantly eolian setting, with intermittent percolation of acidic, oxidizing, and saline groundwater (*4*, *5*). The orbiting spectrometers OMEGA and CRISM have identified other localities across the martian surface that boast thick successions of layered rock rich in Mg and Ca sulfates (*6*). Evaporite minerals in martian meteorites and Fe-sulfate–rich soils analyzed at Gusev Crater provide still further evidence for acid saline conditions (*7*, *8*). By itself, the low pH inferred for martian brines need not have imposed a barrier to life (*1*). What, however, were the consequences of salinity?

At the high solute concentrations needed to form evaporite minerals, water is, to a large degree, made chemically unavailable by ion hydration. As a result, with increasing salinity, biological activity sharply decreases. Quantitatively, the chemical availability of liquid water can be expressed in terms of its activity (a_{H_2O}) (*9*). The a_{H_2O} of pure water is 1.0, a value that decreases with increasing salinity. The a_{H_2O} of terrestrial seawater is 0.98, and the a_{H_2O} of most waters weathering Earth's continental crust falls between 0.98 and 1.0. Most organisms cannot grow at $a_{H_2O} \sim 0.9$, and few are known to tolerate $a_{H_2O} < 0.85$ (*10*). A few extreme eukaryotes fungi and archaea can live in NaCl-saturated solutions with an $a_{H_2O} = 0.75$ (*10*), and a single fungus, *Xeromyces bisporus*, has been shown to grow at $a_{H_2O} = 0.61$ in a high-sugar food (*10*, *11*). This represents the effective habitability limit for terrestrial organisms, but the biological stresses of organic solutes differ from those imposed by inorganic salts, and so the limiting a_{H_2O} could be higher for organisms in inorganic saline systems (*10*). Recently improved thermodynamic models allow us to calculate a_{H_2O} for martian surface environments and so constrain the probability that life arose and persisted there (*12*).

As evaporation proceeds, precipitating saline minerals act as robust markers for ambient a_{H_2O}. The sequence of precipitating minerals is itself controlled by the chemistry of initially dilute waters at the outset of evaporation (*13*). Because fluids on Mars chemically weathered a basaltic crust, the chemistry of dilute martian waters would have been distinct from that of most waters on Earth (*14*). Constraints on the cation chemistry associated with this process come largely from experimental and theoretical studies on the chemical weathering of martian basalt (*15*) [supporting online material (SOM) text].

Our results show that the evaporation of dilute martian waters results in distinct saline mineral assemblages, causing some minerals that are common in terrestrial settings to precipitate at lower a_{H_2O} values than they do on Earth (*16*). For example, halite does not precipitate from martian waters until $a_{H_2O} \leq 0.50$ because of the low abundance of Na released from basaltic weathering. On this basis, the identification of halite at the martian surface (*17*) indicates extreme salinity and brines that would not be inhabitable by known terrestrial organisms.

Temperature and anion content also control the a_{H_2O} of martian brines. The effect of temperature is minor near a temperature (T) > 0°C; a_{H_2O} might increase by ~0.03 to 0.05 over the range of 25° to 0°C. When freezing occurs and equilibrium between ice and surrounding brine is maintained, a_{H_2O} will be controlled by temperature and the amount of ice formed. Thus, in water ice–bearing areas on Mars, the a_{H_2O} of brine phases can be predicted by temperature alone (*18*) (fig. S4).

The proportional anion abundances of dilute evaporating waters exert one of the largest controls on a_{H_2O}. Unlike the principal cations in martian brines, major anions originate ultimately from volcanic degassing. At Meridiani, in situ chemical analyses suggest that the initial S/Cl molar ratio of groundwater brines ranged from ~6.0 to 30.0 (*19*). Here we focus on three important anion species and how changing their relative proportion before evaporation affects a_{H_2O}. Our calculations show that the effect of the SO_4/Cl ratio is most important, so that a decreasing ratio leads to progressively lower a_{H_2O} upon evaporative concentration (*20*) (fig. S1). We calculate that for martian waters with an initial molar SO_4/Cl = 6.0, halite precipitates when $a_{H_2O} = 0.48$. At a SO_4/Cl ratio of 1.0, halite precipitates when the $a_{H_2O} = 0.39$.

For Meridiani Planum, a_{H_2O} can be constrained separately for evaporation that occurred before sediment transport and deposition (Fig. 1) and for brine evolution during diagenesis. Evaporating fluids were initially generated by basaltic weathering (*14*); all major products initially formed by evaporation are probably represented in the Meridiani outcrop because its bulk composition is largely basaltic (*4*, *14*).

The initially precipitated Mg sulfate phase is not precisely identified in Meridiani rocks. Orbital spectroscopy of the surrounding region has identified kieserite ($MgSO_4{\cdot}H_2O$) and other polyhydrated sulfates, for which a number of Mg sulfate hydrates are candidates (*6*). Because of this uncertainty, we considered the a_{H_2O} associated with the precipitation of various Mg sulfate hydrates (*21*). Epsomite precipitation places a maximum on a_{H_2O} at 0.78 (Fig. 1), with hexahydrite and kieserite precipitating at 0.62 and 0.51, respectively (SOM text). Because it represents the most conservative case with respect to habitability, we focus on epsomite here.

Diagenetic events at Meridiani are recorded by detailed textures viewed with the Microscopic Imager. Secondary crystal moldic porosity (or "vugs") in some beds records the syndepositional growth and subsequent dissolution of a soluble mineral. This mineral was preferentially removed by infiltrating groundwater, but much of the primary sedimentary fabric was preserved (Fig. 2). From these textures and the observation of abundant Mg sulfate in the outcrop, we infer that groundwater was at or near saturation with respect to a soluble Mg sulfate mineral (*4*, *14*). The infiltration of dilute water would largely have removed this soluble component, obliterating sedimentary features, which did not occur (Fig. 2). Instead, a variety of recrystallization textures and multiple generations of cement were left behind (*4*).

It has been suggested that the moldic porosity in Meridiani sediments reflects oxidation of a syndepositional Fe^{2+}-sulfate mineral such as melanterite ($Fe^{2+}SO_4{\cdot}7H_2O$) (*4*, *14*). Our calculations show that at 25°C, saturation with respect to epsomite and melanterite in this system occurs at an $a_{H_2O} = 0.78$, similar to the evaporation sequence described above. Oxidation of the soluble Fe^{2+} component to Fe^{3+}-bearing oxides and sulfates (i.e., jarosite) has the overall effect of increasing the a_{H_2O} to 0.86 while still maintaining epsomite saturation. Alternatively, the incongruent melting of meridianiite ($MgSO_4{\cdot}11H_2O$) to epsomite and water has been proposed as a mechanism for creating moldic porosity (*22*). The presence of this mineral before deposition and diagenesis

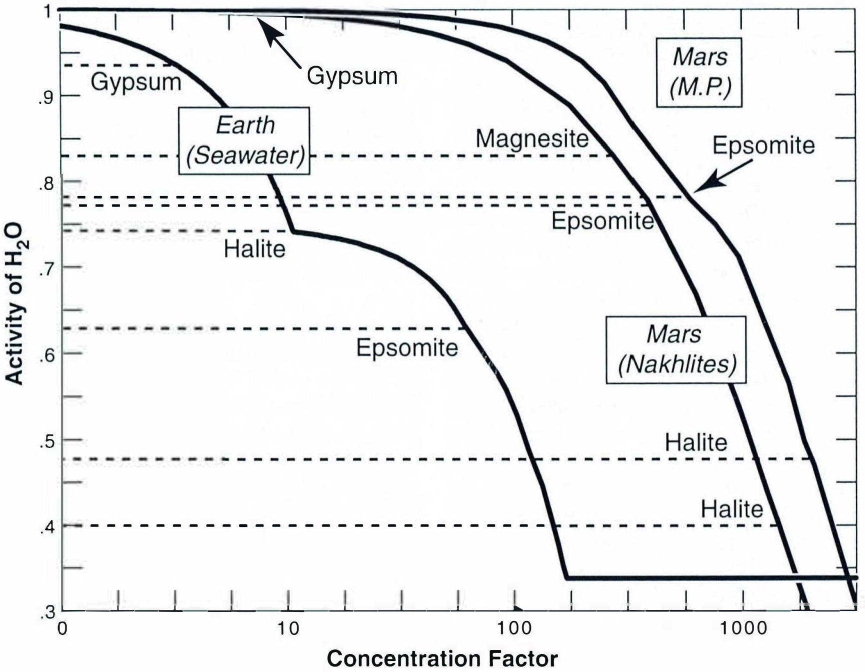

Fig. 1. Calculated mineral precipitation and a_{H_2O} values as a function of evaporative concentration. The blue line represents modern terrestrial seawater evaporation. The red line represents the evaporation of a basaltic-weathering derived fluid most representative of inferred evaporation processes at Meridiani Planum. The green line represents the evaporation of a similar fluid but with an anion concentration that gives rise to the saline mineral assemblage observed in the Nakhla meteorite (and other members of the nakhlite meteorite class).

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