Biogenic Methane, Hydrogen Escape, and the Irreversible Oxidation of Early Earth

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The low O_2 content of the Archean atmosphere implies that methane should have been present at levels $\sim 10^2$ to 10^3 parts per million volume (ppmv) (compared with 1.7 ppmv today) given a plausible biogenic source. CH_4 is favored as the greenhouse gas that countered the lower luminosity of the early Sun. But abundant CH_4 implies that hydrogen escapes to space (↑ space) orders of magnitude faster than today. Such reductant loss oxidizes the Earth. Photosynthesis splits water into O_2 and H, and methanogenesis transfers the H into CH_4. Hydrogen escape after CH_4 photolysis, therefore, causes a net gain of oxygen [$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2 \rightarrow CO_2 + O_2 + 4H(\uparrow \text{space})$]. Expected irreversible oxidation ($\sim 10^{12}$ to 10^{13} moles oxygen per year) may help explain how Earth's surface environment became irreversibly oxidized.

The rise of atmospheric O_2 about 2.4 to 2.2 billion years ago (Ga) (*1*, *2*) changed the course of biological evolution. Yet explaining why O_2 rose at that time has remained elusive, given that bacterial oxygenic photosynthesis was present hundreds of millions of years earlier, before 2.7 Ga (*3*) and possibly since 3.8 to 3.5 Ga (*2*, *4*, *5*). Oxygenic photosynthesis splits water into O_2 and a reductant, H. Hydrogen is used to reduce CO_2 for biosynthesis of organic matter. Nearly all photosynthesized organic matter (today, ~99.9% of $\sim 9000 \times 10^{12}$ mol C year^{-1}) recombines with O_2 via decay or respiration (*6*, *7*). Conventional thinking has focused on the burial of organic carbon as the means of separating photosynthetic reductant from O_2, thereby enabling O_2 to accumulate at the surface. However, the small flux of organic carbon that escapes oxidation through burial in sediments [currently $\sim 10^{13}$ mol C year^{-1} (*6*)] would only cause atmospheric O_2 to rise if the burial rate exceeded the rate of O_2 consumption by reductants supplied to the atmosphere and ocean by geologic processes. Today, these rates appear balanced, with no atmospheric O_2 increase (*6*). Moreover, atmospheric O_2 only increases if reductant that is buried at a preferential rate relative to oxidized material does not later return to the atmosphere or ocean, canceling the O_2 gains (e.g., by reduced metamorphic gases or dissolution of uplifted, reduced continental sediments). The early environment was sufficiently reducing to scavenge O_2 (*2*), so reductant had to be removed preferentially relative to oxidized species and irreversibly to oxygenate the environment permanently. However, no consensus theory has yet emerged to explain why O_2 rose long after oxygenic photosynthesis evolved (*5*), and all current hypotheses are problematic (*8*).

We describe an overlooked biogeochemical mechanism relevant to Earth's redox history: the coupling of early oxygenic photosynthesis to the escape of H to space. H escape provides an alternative to organic burial for removing photosynthetic reductant; H escape is irreversible, whereas metamorphism and continental erosion recycle the reducing power of buried organic matter. In the biosphere, H is transferred from photosynthetic organics to CH_4 by methanogenesis. When CH_4 is decomposed in the upper atmosphere by ultraviolet (UV) radiation, H escapes to space forever. The overall chemistry is $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2 \rightarrow CO_2 + O_2 + 4H(\uparrow \text{space})$, where the first reaction sums photosynthesis and methanogenesis. Currently, Earth gains oxygen by CH_4-induced H escape at a negligible rate $\sim 10^{10}$ mol O_2 year^{-1} because the rate depends on the magnitude of the atmospheric mixing ratio of CH_4 (f_{CH_4}), which today is only 1.7 ppmv.

However, CH_4 would have been an important trace atmospheric constituent before the rise of O_2. Today, the large biogenic flux of CH_4 to the atmosphere is oxidized, limiting f_{CH_4} (*9*). But in the low-O_2 Archean, the kinetic fates of biogenic O_2 and CH_4 would have been reversed. O_2 would have been rapidly consumed and CH_4, long-lived. Rapid reaction of O_2 with reduced metamorphic and volcanic gases and with upwelling oceanic cations like Fe^{2+} would have buffered O_2 to trace levels (*10*). Also, organic carbon uplifted onto continents and washed to the ocean would have been consumed aerobically to produce CO_2 or anaerobically to make CH_4 plus CO_2, given that Archean elemental carbon is found in biologically mediated fine-grained shales (fixed from CO_2) rather than in detrital form (*11*). An Archean methanogen biosphere is suggested by biochemistry (*12*) and carbon isotope evidence (*13*–*15*). Photochemical models suggest Archean f_{CH_4} ~200 to 3000 ppmv (*16*–*18*) if the biogenic CH_4 production rate were 0.1 to 1 times that of the present.

Abundant atmospheric CH_4 is also the most plausible explanation for Archean greenhouse warming (*17*). A large greenhouse effect is needed to explain the temperate Archean climate when solar luminosity was 20 to 30% lower than today (*19*). A partial pressure of carbon dioxide (pCO_2) a few hundred to 1000 times larger than today has been postulated (*20*) but is improbable for several reasons. Paleosols indicate that pCO_2 was an order of magnitude too low to counter a fainter Sun at 2.75 Ga (*21*). The mineralogy of banded iron formations also suggests that $pCO_2 < 0.15$ bar at 3.5 Ga (*22*). Abundant Archean marine limestone indicates calcite supersaturation then, as now (*7*). If pCO_2 were high, oceanic Ca^{2+} should have been depleted, but evaporitic gypsum (*23*) suggests otherwise. Also, carbonatization of the seafloor should have lowered pCO_2 to levels inconsistent with a dominant greenhouse role (*24*). Further, Archean geochemical data do not indicate levels of acid weathering expected for $pCO_2 > 100$ times present (*25*). Consequently, the theory of Archean CH_4 greenhouse warming (Fig. 1A) has become favored (*15*–*18*, *21*, *24*). High CH_4 is consistent with relatively low pCO_2 because if a large greenhouse enhancement by CO_2 were added to warming dominated by CH_4, CO_2 would be consumed in negative feedback by temperature-dependent weathering of continental silicates. A CH_4-mediated climate can be stabilized in negative feedback with O_2; e.g., increasing f_{CH_4} causes greenhouse warming, which increases weathering, sedimentation, and, ultimately, organic burial rates. The latter, in turn, increases O_2, which lowers f_{CH_4}.

Climatologically important CH_4 (Fig. 1A) induces rapid escape of H to space. H escapes from the base of Earth's exosphere (~300- to 500-km altitude), where H atoms are the only H species (*26*, *27*). Several processes rapidly depopulate H atoms from the exosphere so that diffusive supply of H from lower levels is the rate-limiting step (*27*). The total concentration of all H-bearing compounds in the lower stratosphere, f_{total} ($= f_{H_2O} + f_{H_2} + 2f_{CH_4} \ldots$) (expressed as H_2 molecules for these calculations) determines the diffusion-limited H escape rate, ϕ_{escape}, given by (*27*):

$$\phi_{escape} = 2.5 \times 10^{13} f_{total} \ (H_2 \text{ molecules cm}^{-2} \text{ s}^{-1}) \quad (1)$$

Today, ϕ_{escape} is trivial (Table 1) because f_{total} is small, given only 3 ppmv water vapor,

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1.7 ppmv CH_4, and 0.55 ppmv H_2 in the lower stratosphere. Upward transport of H in H_2O, in particular, is limited by a "cold trap" at the tropopause where water condenses. Because such a cold trap is a general feature of paleoatmospheres, oxygen production by abiotic H escape from water vapor can be neglected (*7*). However, CH_4 is not cold trapped and increased H escape is unavoidable with increased f_{CH_4}. If Archean f_{CH_4} were ~1000 ppmv (*16–18*), ϕ_{escape} would be ~300 times higher than today's flux (Table 1). Large CH_4-induced H escape rates and significant global oxidation rates are general consequences of a high Archean f_{CH_4} (*28*).

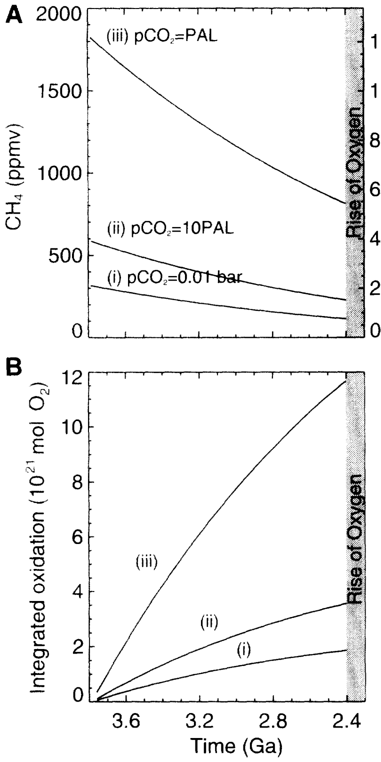

Fig. 1. (**A**) The calculated mixing ratio of CH_4 (left ordinate axis) needed to maintain a surface temperature of 290 K on early Earth against the lower luminosity of the young Sun. We used the radiative modeling of (*17, 18*). The mean global temperature in the Archean is assumed to be similar to that of the present day, given the absence of extensive glaciation in the Archean and constraints from Archean evaporites (*7, 23*). CH_4 mixing ratios are calculated at three fixed levels of pCO_2 as indicated, where PAL indicates present atmospheric level ≈ 0.0003 bar. The upper pCO_2 limit, pCO_2 = 0.01 bar, is derived from paleosols for 2.2 to 2.8 Ga at 290 K (*21*) and yields a lower limit on CH_4. The irreversible oxidation fluxes due to escape of hydrogen, corresponding to particular levels of CH_4, are expressed as molar O_2 equivalents per year (right ordinate axis). We end calculations at 2.4 to 2.3 Ga, assuming that CH_4 levels collapsed upon the rise of atmospheric O_2. (**B**) Integrated oxidation due to CH_4-induced H escape to space, using the three atmospheric CH_4 levels from (A), shown with matching labels. Cumulative oxidation and the observed molar oxygen inventory in the continental crust (Table 2) are comparable.

Escape of H to space oxidizes Earth as a whole. Oxidation is expressed in the geochemical reservoir where the H originates, although the resultant oxidized species may subsequently be transported to other reservoirs. We explain how oxidation results from CH_4-induced H escape in three cases: (i) when CH_4 originates from organic matter produced by oxygenic photosynthesis, (ii) when CH_4 derives from organic matter produced by anoxygenic autotrophic metabolisms, and (iii) when CH_4 derives from mantle H.

In (i), oxygen is gained irreversibly because photosynthetic splitting of water produces O_2 and H, and CH_4-mediated escape removes the H forever. This process is schematically represented in Eqs. 2 through 5. Oxygenic photosynthesis can be summarized as

$$CO_2 + H_2O = CH_2O + O_2 \qquad (2)$$

where CH_2O represents organic matter. Production of CH_4 mainly derives from symbiotic communities of heterotrophs and methanogens that decompose organic matter (*13*).

$$2CH_2O = CH_4 + CO_2 \qquad (3)$$

H escape to space via CH_4 can be represented as follows, noting that the detailed photochemistry (*16*) is rather more complex.

$$CH_4 + h\nu \rightarrow C + 4H(\uparrow \text{space}) \qquad (4a)$$

$$C + O_2 = CO_2 \qquad (4b)$$

Thus, the combined effect of the early biosphere, using the processes of oxygenic photosynthesis (Eq. 2), methanogenesis (Eq. 3), and H escape (Eq. 4), is described by the sequential sum of these processes [(2 × Eq. 2) + Eq. 3 + Eq. 4]. This gives the overall chemical transformation of the crustal system:

$$2H_2O + \text{"the biosphere"} + h\nu \rightarrow O_2 + 4H(\uparrow \text{space}) \qquad (5)$$

Consequently, the irreversible gain of oxygen from CH_4-induced H escape derives from water split by oxygenic photosynthesis. A more circuitous route to oxygen gain occurs when buried organic matter devolatilizes by diagenesis or metamorphism to produce H_2 (e.g., via $CH_2O + H_2O = 2H_2 + CO_2$) or CH_4 (via $2CH_2O = CH_4 + CO_2$). During the Archean, if methanogens produced CH_4 by consuming metamorphic H_2, or if CH_4 or H_2 fluxed directly from decomposed buried organic matter, the net effect of Eq. 5 would still apply.

Case (ii) concerns CH_4 originating from anoxygenic photoautotrophs or chemoautotrophs. Such prokaryotes use H_2, reduced sulfur, or Fe^{2+} as electron donors in biosynthesis (e.g., $H_2S + CO_2 + h\nu \rightarrow CH_2O + H_2O + S$). If CH_4 were derived from such organic matter, H escape would leave behind oxidized S or Fe, contributing to net crustal oxidation (though free O_2 is not produced), provided that the electron donor originated from the crust (e.g., metamorphic H_2S). If the electron donor fluxed from the mantle, case (iii) would apply.

Case (iii) concerns methanogenic CH_4 derived from mantle hydrogen in volcanic gases. Volatile fluxes to the atmosphere have probably been dominated by recycling of crustal sedimentary rocks since the early Proterozoic or earlier via metamorphism or volcanism (*29, 24*). Volcanic gases derive from magma, whereas metamorphic gases are not directly associated with a silicate melt. Mantle minerals buffer the redox state of volcanic gases, and when H is exported mantle min-

Table 1. Earth's oxygen fluxes.

Type of flux	Amount ($\times 10^{12}$ mol O_2 year^{-1})	Action
Modern organic carbon burial flux*	10 ± 3	Production
Modern pyrite burial flux†	~1.7	Production
Modern Fe^{3+} subduction flux to the mantle‡	0.5 to 1.9	Loss
Modern continental oxidative weathering flux*	7.5 ± 1.7	Loss
Modern flux of reduced volcanic and metamorphic gases*	3 ± 1	Loss
Modern net photosynthetic flux to the atmosphere (assuming the burial fluxes and oxidative losses are balanced by negative feedbacks)*	~0	Net change
Modern gain from H escape to space§	0.02	Absolute gain
Archean gain from H escape to space, with 100 to1000 ppmv CH_4§	0.7 to 7.0	Absolute gain

*From (*6*). †FeS_2 is produced by bacteria that use sulfate and Fe^{3+} as oxidants, with 15/8 moles of O_2 liberated per mole of sulfur (*60*). ‡The estimated net flux to the mantle is 3.8×10^{14} g Fe^{3+} year^{-1} (*36*). Fe^{3+} derives from hydrothermal alteration of oceanic basalt; i.e., $22FeO + 2SO_4^{2-} + 4H^+ = FeS_2 + 7Fe_3O_4 + 2H_2O$. Because 14 moles of Fe^{3+} are subducted for 2 moles of SO_4^{2-}, the net O_2 flux to the mantle is $(3.8 \times 10^{14}$ g/56 mol Fe^{3+} year$^{-1})/14 = 0.5 \times 10^{12}$ mol O_2 year^{-1} if the SO_4^{2-} had been derived from oxidation of SO_2 or 1.9×10^{12} mol O_2 year^{-1} if the SO_4^{2-} had been derived from oxidation of H_2S. §Calculated from Eq. 1.

erals are oxidized to satisfy redox balance (*30*). Redox-sensitive elements in igneous rocks show that the oxygen fugacity of volcanic gases has not changed by more than 0.5 $\log_{10}$ units since 3.6 Ga (*31*), presumably because of effective mantle buffering. These data rule out the suggestion that mantle oxidation was an important factor in the rise of O_2 (*30*, *32*). Although mantle H can escape directly to space, biogenic CH_4 may have helped prevent sequestration of mantle reductant into the Archean crust. If mantle H had transferred reducing power to solids in the crust (e.g., if H were efficiently scavenged by bacteria to reduce CO_2 to organic matter), the crust could have become gradually more reduced. However, fermentation of organic matter to CH_4 and resultant H escape would allow mantle H to be lost to space.

In all cases discussed above, Earth's overall oxidation state increases. Case (iii) oxidizes the mantle. Cases (i) and (ii) oxidize the crust (e.g., as Fe_2O_3 or SO_4^{2-}), which, in the long-term, must shift kinetics to favor the survival of free O_2. Free O_2 is only produced in case (i), which includes oxygenic photosynthesis. Oxygenic photosynthetic bacteria extract H from water, making them independent of abiotic sources of reductants; they would have dominated global productivity once they evolved (*33*), rendering the other cases inconsequential for effecting significant crustal redox changes. Biogenic CH_4 would be the major H-bearing species in the Archean stratosphere (*16*–*18*), so Eq. 1 can be rewritten with $f_{\text{total}} \approx 2f_{CH_4}$

$$\phi_{\text{oxidation}} \approx 13.1 f_{CH_4} \quad (O_2 \text{ mol m}^{-2} \text{ year}^{-1}) \tag{6}$$

Thus, if f_{CH_4} in the Archean atmosphere were ~100 to 2000 ppmv (Fig. 1A), the effective flux of O_2 into the crust due to CH_4-induced H escape would be (0.7 to 14) $\times 10^{12}$ mol year^{-1}. This rate is comparable in magnitude to the (reversible) modern O_2 flux due to organic burial of $\sim 10^{13}$ moles O_2 year^{-1} (Table 1) and would produce (0.7 to 14) $\times 10^{21}$ mol O_2 in $\sim 10^9$ year, comparable to the continental crustal reservoir of excess oxygen (Table 2).

Large oxygen inventories include the continental crust (Table 2) and mantle. The continental crust's excess oxygen mostly resides in altered and metamorphosed igneous rocks. Archean basalts have a weight ratio $Fe^{3+}/\Sigma Fe$ several times greater than fresh basalt, for which $Fe^{3+}/\Sigma Fe \sim 0.07$. Metamorphic oxidation of crustal ferrous minerals by water alone requires extreme volumes of water (e.g., ~1500-g water per 1-g magnetite to oxidize magnetite to hematite at 5 kbar and 630°C), so SO_4^{2-} or O_2 are often implicated as oxidants whenever Fe^{3+} is observed to increase (*34*). Transfer of the oxidizing power of SO_4^{2-} to Fe^{3+} is consistent with low SO_4^{2-} in Archean oceans relative to today's oceans (*35*). In the ocean, continuous oxidation facilitated by CH_4-induced H escape would have produced Fe^{3+} from oceanic Fe^{2+}. Thus, O_2 would have been exported to the mantle through past subduction of Fe^{3+} (Table 2). Ferric oxides are denser than mantle material with a refractory tendency for deep subduction (*36*), so it is probable that surviving Archean iron formations are a mere fraction of those originally deposited.

The oxidation caused by H escape for greenhouse CH_4 levels (Fig. 1A) can be integrated over time and compared with the crustal oxidized inventory (Table 2). For the f_{CH_4} required for warming the early Earth, cumulative oxidation [Fig. 1B, curves (i) and (ii)] is consistent with estimates of the continental crust's inventory of oxygen (Table 2).

Net oxidation of crustal rocks in the past would have increasingly enhanced the kinetic stability of atmospheric O_2. Today, most degassed carbon volatiles are recycled via metamorphism rather than volcanism. The ratio of metamorphic to volcanic gas fluxes has likely increased through time (*7*, *24*). Thus, models that equate the early Earth's H escape flux to fluxes of reductant from the mantle (*30*, *32*) are incorrect. These models neglect metamorphic and continental sources of reductant, providing no explanation for the net oxidized state of crustal reservoirs in Table 2. If crustal volatile recycling dominates, to first order CH_4-induced H escape to space would oxidize the crust by Eqs. 5 and 6. Because the residence time of Archean O_2 would be small (*10*, *16*), O_2 would be sequestered into oxides (e.g., Fe_2O_3, SO_4^{2-}, CO_3^{2-}). Unlike volcanic gases, the average oxidation state of metamorphic gases is independent of mantle buffering and is controlled largely by the oxidation state of the original sediments (*34*, *37*). Thus, the oxidation state of Archean metamorphic gases would have increased over time as crustal rocks became more oxidized (*37*). Reductants released by metamorphism (H_2, CO, H_2S, etc.) would remove atmospheric O_2, enabling high f_{CH_4} (*10*) and rapid H escape. Oxidation resulting from such H escape would be expressed inside the crust where the reductant originated. The surface would remain weakly reducing, although river fluxes of reductant to the ocean from weathering would presumably have declined with increasing oxidation of uplifted rocks. However, the details of metamorphic or weathering redox changes are superfluous: Le Châtelier's principle demands that atmospheric and oceanic O_2 sinks decrease as the crust is irreversibly oxidized via CH_4-induced H escape. This is consistent with the prevalence of methanotrophs in the late Archean using increasing levels of dissolved SO_4^{2-} or O_2 (*12*). Then, in the early Proterozoic, peak iron formation deposition occurred (*7*) and sulfate-reducing bacteria became increasingly ubiquitous (*35*).

Table 2. Oxidized and reduced reservoirs in Earth's continental crust. The Earth's exterior contains Fe_2O_3 and SO_4^{2-}, which arose via oxidation, and atmospheric O_2. Oxidized species are expressed in terms of the O_2 moles required for their production; e.g., each mole of Fe^{3+} needed 1/4 mole O_2 to be produced from Fe^{2+}. Reduced species are expressed in terms of O_2 moles required for their consumption. By, billion years; R_{OX}, oxygen in the continental crust; AOS, atmosphere, ocean, and sedimentary; R_{AOS}, oxygen in the AOS system; R_{redC}, reduced carbon in the continental crust.

Species and reservoir	Amount ($\times 10^{21}$ mol O_2 equivalent)	Size comparisons
	Oxidized species	
O_2 in the atmosphere and ocean*	0.037	$0.07 \times R_{AOS}$
Fe_2O_3, SO_4^{2-}, and O_2 in the AOS system†	0.55	R_{AOS}
Total Fe^{3+} in the continental crust‡	1.7 to 2.6	(3.1 to 4.7) $\times R_{AOS}$
Total R_{OX} (excluding oxygen transferred into carbonates)	2.0 to 2.9	(1.5 to 2.2) $\times R_{redC}$
Net subducted Fe^{3+} loss over 4 By§	2.0 to 7.6	1.5 to 5.8 $\times R_{redC}$
Carbonate in the continental crust‖	2.2 to 7.1	
	Reduced species	
Reduced carbon in the AOS system¶	0.56	
Reduced carbon in felsic instrusives, gneisses, schists and felsic granulites¶	<0.78	
Total R_{redC}	<1.3	R_{redC}
Total reduced carbon delivered during 4.4 to 3.8 Ga#	~1	$\sim R_{redC}$

*From (*6*). †From (*61*). ‡Much of this Fe^{3+} is in continental basalt that has been oxidized metamorphically or hydrothermally within the crust (*36*). §Crude estimate assuming today's net subduction rate (Table 1), uniformly extrapolated over 4 By, without accounting for the opposing influences of lower oceanic sulfate and higher seafloor spreading on early Earth. ‖Lower estimate from (*62*), upper estimate from (*61*). ¶From (*62*). #The total accreted mass from impact bombardment would be on the order of 10^{21} kg (*63*). Celestial dynamics and D/H in the ocean suggest that impacts were due to asteroids, not comets. To arrive at this estimate, we assumed ~1% average reduced carbon content of asteroids.

That the crust is at a higher oxidation state than the mantle from which it was derived suggests irreversible oxidation. Crustal oxygen fugacity varies by orders of magnitude from fayalite-magnetite-quartz (FMQ) to hematite-magnetite (HM) buffer levels (*38*), whereas the upper mantle is near FMQ (*39*). Furthermore, photosynthesis produces organic carbon balanced by oxides of sulfur and iron (after loss of O_2), so buried organic carbon should balance oxidized materials in the crust if no H escape occurred. However, estimates of the continental crustal inventory show that oxidized species exceed reduced carbon by a factor of 1.5 to 2.2 (Table 2). This budget excludes oxidized carbon, some of which may have started out reduced; i.e., when reduced carbon delivered by impact bombardment during 4.4 to 3.8 Ga is subtracted from the reduced inventory, the dominance of oxidized species increases. Time-integrated subducted losses of Fe^{3+} to the mantle may also further increase the redox imbalance (Table 2). A greater oxidized versus reduced inventory can be reconciled only by H escape, or preferential subduction of organic carbon relative to oxidized species, or both. Subduction of ^{12}C-enriched graphitic carbon relative to carbonate is unlikely because marine carbonates do not become increasingly ^{12}C-depleted with geologic time (*40*). But we cannot discount enhanced subduction of graphitic carbon relative to subduction of oxidized species as a whole. Any irreversible, preferential loss of reductant into the mantle would be identical in its crustal redox effect to H escape to space. Nonetheless, oxidation due to CH_4-induced H escape is chemically expected and can reconcile the observed redox inventory on its own. Other geochemical evidence of CH_4-induced H escape may reside in low values of D/H (deuterium/hydrogen) inferred for Archean seawater (*41*).

References and Notes

1. At ~2.4 to 2.2 Ga, the onset of red beds, oxidized paleosols, a step change in mass-independent sulfur isotopes, and the oxidative loss of detrital pyrite, siderite, and uraninite all indicate an "oxic transition" in the atmosphere (*2*, *42*–*45*). The partial pressure of oxygen (pO_2) was <0.0008 atm before the transition and >0.03 atm afterward (*42*).
2. H. D. Holland, *Geochem. News* **100**, 20 (1999).
3. J. J. Brocks, G. A. Logan, R. Buick, R. E. Summons, *Science* **285**, 1033 (1999).
4. R. Buick, *Science* **255**, 74 (1992).
5. Biomarkers derived from oxygenic cyanobacteria and from eukaryotic sterols are present at 2.7 Ga (*3*). Localized biological O_2 sources are apparent at 2.7 to 3.0 Ga from stromatolites (*4*). On the basis of $\delta^{15}N$ values in Precambrian organic matter, it is estimated that oxygenic photosynthesis began to be important at ~3.4 to 2.7 Ga (*2*).
6. H. D. Holland, *The Chemistry of the Atmosphere and Oceans* (Wiley, New York, 1978).
7. ———, *The Chemical Evolution of the Atmosphere and Oceans* (Princeton Univ. Press, Princeton, NJ, 1984).
8. One explanation is that as geothermal heat declined, the reducing volcanic flux dwindled, allowing O_2 to rise. However, increased past volcanic outgassing would have also injected proportionately more CO_2. Carbon isotopes from 3.5 Ga onward show that a roughly constant fraction, f_{org}, (~20%) of the CO_2 flux into the biosphere was fixed biologically and buried as organic carbon with the remainder buried as carbonate (*40*). If f_{org} were constant, increased outgassing in the past cannot, on its own, explain the oxic transition because as one goes back in time, O_2 production due to organic burial would have risen in parallel with O_2 losses. A second explanation of the rise of O_2 recognizes the previous problem by invoking a gradual shift of high-temperature volcanic gases from reduced to oxidized (*30*, *32*). However, this hypothesis conflicts with recent data (*31*, *39*, *46*). A third hypothesis argues for an increase in the rate of organic burial linked to growth in continental platforms suitable for burial (*47*). It is suggested that carbon isotopes from 2.6 to 2.0 Ga indicate burial fractions of organic carbon increasing from f_{org} ~ 10 to >20%. Several uncertainties arise. First, during 3.5 to 2.9 Ga, f_{org} was normal, ~20% (*40*). Second, anomalously low organic carbon isotopic values at 2.8 to 2.6 Ga appear to be methanotrophic (*12*–*15*) so that an inference of increasing carbon burial rates starting at 2.6 Ga using running averages of isotopic data is problematic. Third, secular continental growth appears increasingly unlikely on the basis of recent geochemical inferences of early continents (e.g., *48*). A fourth hypothesis suggests that carbonate isotope excursions from 2.05 to 2.25 Ga were due to a massive pulse of organic burial that caused the rise of O_2 (*2*). However, the inferred amount of buried organic matter is missing from coeval geologic strata (*49*). The isotope excursions may have occurred after the oxic transition (*43*), and no convincing explanation is offered for why such massive organic burial was concentrated into 200 million years (My) of the early Proterozoic. Furthermore, such massive buried organic carbon (unless it had been subducted irreversibly) would, in the long-term geological cycle, devolatilize to produce reducing metamorphic gases or would be re-exposed, consuming O_2 at enhanced rates and canceling O_2 gains. A pulse of organic burial should merely cause atmospheric O_2 to rise and decay [like in the Paleozoic (*50*)], not accumulate irreversibly.
9. Today, the atmosphere receives ~3×10^{13} mol CH_4 $year^{-1}$, noting that much additional CH_4 is oxidized by bacteria (e.g., with sulfate) before reaching the atmosphere. In a low-sulfate Archean ocean (*35*), it is possible that proportionately more CH_4 reached the atmosphere. Atmospheric oxidation rates of CH_4 are controlled by the initial step in the oxidation process that today takes ~7 to 12 years: $OH + CH_4 = CH_3 + H_2O$. Oxidation becomes complete in the upper atmosphere, converting CH_4 into CO_2 and photodissociated fragments of water with the net reaction $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$.
10. Steady-state concentrations of atmospheric gases bear little resemblance to their relative fluxes into the atmosphere because different destruction rates control each gas. After accounting for back reaction of O_2 and CH_2O via respiration and decomposition, fluxes of biogenic O_2 and CH_4 to the atmosphere are stoichiometrically balanced when photosynthesis and methanogenesis are combined (Eq. 2 × 2 + Eq. 3 results in $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$). However, O_2 is much more reactive than CH_4. Thus, in the weakly reducing Archean environment, O_2 would be lost rapidly to form soluble or insoluble oxides, whereas inert CH_4 would remain in the air at a much higher equilibrium concentration than today (*16*). O_2 would react rapidly with reduced gases (from volcanism, metamorphism, and diagenesis), upwelling ocean waters containing Fe^{2+}, and riverine fluxes of dissolved reductants (e.g., organic complexes). A rough pO_2 can be estimated by assuming that only oxidation of oceanic Fe^{2+} buffered O_2, neglecting all other losses (to H_2, CO, etc.). If Fe^{2+} were ~3 ppm in the deep pre-oxic ocean (*51*), a mean oceanic upwelling rate of 5 m $year^{-1}$ gives a potential sink for O_2 of $(3 \times 10^{-6}/56 \text{ mol cm}^3) \times (5 \times 10^2 \text{ cm year}^{-1}) \times (3.6 \times 10^{18} \text{ cm}^2)/4 \sim 10^{13}$ mol O_2 $year^{-1}$, similar to modern organic burial rates. Thus, it is reasonable to estimate pO_2 by balancing Fe^{2+} oxidation rates, ϕ_{ox} (mol O_2 m^{-2} $year^{-1}$), with an assumed organic burial O_2 flux, F_{O_2}, similar to modern values ~0.02 mol O_2 m^{-2} $year^{-1}$. Using $\phi_{ox} \approx 0.25\rho_w H_s k [OH^-]^2 (pO_2) [Fe^{2+}] = F_{O_2}$ (*52*) with rate constant $k \approx 5.3 \times 10^{17}$ mol^{-2} kg^2 atm^{-1} $year^{-1}$, seawater density $\rho_w = 1025$ kg m^{-3}, and mixed layer depth $H_s \sim 100$ m, we deduce $pO_2 \leq 10^{-6}$ bar for pH ≥ 7, consistent with paleosol constraints (*2*). The residence time of atmospheric O_2 would therefore have been approximately days. Archean CH_4 levels from photochemical models are ~1000 ppmv (*16*), yielding a residence time of $(1.8 \times 10^{20} \text{ mol air} \times 10^{-3})/(3 \times 10^{13} \text{ mol CH}_4 \text{ year}^{-1}) = 6000$ years, using the present biogenic flux of CH_4 (*9*). This is the reverse of today, for which CH_4 has a residence time of 7 to 12 years (*9*) and O_2 cycles through the biosphere in ~6000 years (*53*).
11. H. D. Holland, in (*7*), p. 353.
12. The presence of CH_4-generating archeabacteria (methanogens) in the Archean is implied by their genetic lineage, which places them close to the earliest common ancestor for all life. Today, methanogens are found in nearly every conceivable anaerobic niche. In the globally anaerobic Archean, habitats would likely abound, given methanogens' tolerance to temperature (2° to 110°C), salinity (freshwater to brine), and pH (3 to 9). CH_4 is somewhat chemically inert and sparingly soluble, so it has proved impossible to detect a geochemical signature of its trace abundance in the rock record. However, methanotrophs—organisms that oxidize methane with O_2 or SO_4^{2-}—are globally indicated in the late Archean by organic carbon isotopes (*13*–*15*). Methanogens fractionate the stable isotopes of carbon (^{13}C and ^{12}C) in favor of ^{12}C. When methanogen CH_4 is consumed by methanotrophs, the carbon is further fractionated, leading to organic carbon much depleted in ^{13}C. At ~2.7 to 2.8 Ga, methanotrophic organic $\delta^{13}C$ implies >20 ppmv CH_4 (*13*, *15*). CH_4 could have been present at higher trace levels throughout the Archean but would have been invisible in the carbon isotope record in the absence of significant methanotrophy, which may have arisen later with increasing local oases of O_2 or SO_4^{2-}. Methanotrophic signatures declined after 2.6 Ga perhaps because of increasing competition with other aerobes for oxidants. Nonetheless, methanogens have continued to provide a large flux of methane to the present day (*9*).
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25. H. D. Holland, in (*7*), p. 185.
26. When temporally averaged, H atoms are mostly removed nonthermally from the exosphere by charge-exchange processes where an ion with excess energy is converted into an atom with excess energy, i.e., $H + H^{+*} \rightarrow H^+ + H^*$, where an asterisk denotes excess kinetic energy. Ion escape is prevented by Earth's magnetic field, but neutralized ions are free to escape. H atoms with escape velocities in the tail of the Maxwell-Boltzmann distribution only contribute 10 to 40% of the escape flux (a proportion known as "Jean's escape"), and the polar wind supports a further contribution.
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28. Some have speculated that a much lower exospheric temperature in the Archean might have diminished H

escape by thwarting thermal escape (*17*). If the early Archean thermopause (the top of the thermosphere or "exobase") were <500 K compared with today's temperature of ~1000 K, the thermal escape of H atoms at the thermopause would have been significantly lowered. However, this speculation does not stand up to scrutiny. Various species (N_2, O, O_2, H, and He) absorb UV radiation and warm the thermosphere. The Archean's lack of O_2 absorption would not cause a colder thermopause than today because extreme UV fluxes (EUV) from the Archean Sun were two to four times higher (*54*). These EUV fluxes easily compensate for lack of O_2 based on detailed calculations of the thermospheric temperature for an anoxic Earth (*55*). Greater pCO_2 could cool the thermosphere radiatively. The mesopause (the cold base of the thermosphere at about ~85-km altitude, where CO_2 cools radiatively) occurs at a pressure level inversely proportional to ${f_{CO_2}}^{0.5}$, where f_{CO_2} is the mixing ratio of CO_2 (*56*). At the upper pCO_2 limit (~0.04 bar) allowed by 2.75 Ga paleosols (*21*), the mesopause would be higher by only ~2 mesospheric scale heights (~10 km) in comparison to today. This altitude is still in the mixed region below the homopause, so diffusive separation in the overlying thermosphere would suppress thermospheric CO_2 abundances and prevent significant thermospheric cooling. The radiative cooling effects of molecular CH_4 on the thermopause can be neglected because CH_4 is photolyzed at lower altitudes (~60 km) and does not reach the thermosphere in a molecular form. So the idea of a cold Archean exobase is unsupported. Equally important, temperature-dependent Jean's escape is a minor process, on average. Nonthermal processes account for 60 to 90% of the H depopulation from the exobase (*26, 27*) and are intimately associated with the Earth's magnetic field. Thus, upward diffusion of H rather than the rate of H depopulation would set the Archean H escape rate from the exobase.

29. H. D. Holland, in (*7*), p. 83.
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31. The oxygen fugacity (fO_2) of the upper mantle does not appear to have changed by more than 0.5 $\log_{10}$ units since 3.6 Ga, based on redox-sensitive vanadium and chromium contents in igneous rocks (*46, 39*). These data contradict the hypothesis that a change in redox state of high-temperature volcanic gases facilitated the rise of O_2 (*30, 32*). Mantle fO_2 can remain constant even with continual net subduction of oxidized species, such as Fe^{3+}, into the mantle over geologic time because of oxygen-buffering assemblages. As long as the mantle's mineral assemblage possesses all of the minerals involved on both sides of the chemical buffering reaction, fO_2 will remain buffered by that assemblage.
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37. The redox state of metamorphic gases (i.e., gases that are not associated with a melt) is controlled by rock chemistry. Redox reactions in many metamorphosed crustal rocks are buffered by ferrous or ferric iron, carbon, or sulfur (*34*). For a given rock buffer, e.g., fayalite-magnetite-quartz (FMQ), low-temperature metamorphic gases tend to be more reducing (with more H_2, CO, etc.) than their volcanic counterparts released at FMQ. When enough oxygen is added to crustal rocks to exhaust buffers, metamorphic gases increase in oxidation state by orders of magnitude. Redox balance requires that the overall oxidation state of metamorphic gases and the metamorphosed rocks they leave behind be preserved. Because the whole sedimentary rock reservoir is recycled with a half-life ~200 My even at present-day erosion rates (*57*), if O_2 were added to Archean sediments and associated crustal rocks, this would have inevitably created a more oxidized overall combination of metamorphic gas and riverine weathering fluxes.
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41. Because of isotopic exchange of old rocks with recent waters, δD of the Archean oceans is poorly constrained [δD is the ratio of deuterium to hydrogen relative to the standard [$^2D/^1H$ (standard)] for standard mean ocean water (SMOW), expressed in parts per thousand. $\delta D = \{[^2D/^1H \text{ (sample)} - {}^2D/^1H \text{ (standard)}]/[^2D/^1H \text{ (standard)}]\} \times 1000$]. Kerogen δD, for example, is especially unreliable. However, Archean gneisses and granites from Swaziland have δD ~30 per mil (‰) lower than in Phanerozoic batholiths, which has proved puzzling (*58*). This might be explained if oceanic crust reacted with an ocean with a δD value closer to –30‰ rather than the present-day value of 0‰ (*59*). Methanogen methane has $\delta D = -150$ to –300‰. If oxygenic photosynthesis coupled to CH_4-induced H escape caused cumulative oxidation ~2.5×10^{21} mol O_2 (see Fig. 1B), 6.3% of the ancient ocean mass would have been lost. In the first approximation that D and H escape according to their proportions in biogenic methane, oceanic δD would increase ~10 to 20‰. Also, any tendency for the lighter H isotope to escape preferentially would further increase δD.
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Josephson Junction Arrays with Bose-Einstein Condensates

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We report on the direct observation of an oscillating atomic current in a one-dimensional array of Josephson junctions realized with an atomic Bose-Einstein condensate. The array is created by a laser standing wave, with the condensates trapped in the valleys of the periodic potential and weakly coupled by the interwell barriers. The coherence of multiple tunneling between adjacent wells is continuously probed by atomic interference. The square of the small-amplitude oscillation frequency is proportional to the microscopic tunneling rate of each condensate through the barriers and provides a direct measurement of the Josephson critical current as a function of the intermediate barrier heights. Our superfluid array may allow investigation of phenomena so far inaccessible to superconducting Josephson junctions and lays a bridge between the condensate dynamics and the physics of discrete nonlinear media.

The existence of a Josephson current through a potential barrier between two superconductors or between two superfluids is a direct manifestation of macroscopic quantum phase coherence (*1, 2*). The first experimental evidence of a current-phase relation was observed in superconducting systems soon after the Josephson effect was proposed in 1962 (*3*), whereas verification in superfluid helium has been presented only recently owing to the difficulty of creating weak links in a neutral quantum liquid (*4, 5*). The experimental realization of Bose-Einstein condensates (BEC) of weakly interacting alkali atoms (*6, 7*) has provided a route to study neutral superfluids in a controlled and tunable environment (*8, 9*) and to implement novel

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