

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

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

The rise of atmospheric O<sub>2</sub> about 2.4 to 2.2 billion years ago (Ga) (1, 2) changed the course of biological evolution. Yet explaining why O<sub>2</sub> 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<sub>2</sub> and a reductant, H. Hydrogen is used to reduce CO<sub>2</sub> for biosynthesis of organic matter. Nearly all photosynthesized organic matter (today, ~99.9% of ~9000 × 10<sup>12</sup> mol C year<sup>-1</sup>) recombines with O<sub>2</sub> 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<sub>2</sub>, thereby enabling O<sub>2</sub> to accumulate at the surface. However, the small flux of organic carbon that escapes oxidation through burial in sediments [currently ~10<sup>13</sup> mol C year<sup>-1</sup> (6)] would only cause atmospheric O<sub>2</sub> to rise if the burial rate exceeded the rate of O<sub>2</sub> consumption by reductants supplied to the atmosphere and ocean by geologic processes. Today, these rates appear balanced, with no atmospheric O<sub>2</sub> increase (6). Moreover, atmospheric O<sub>2</sub> 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<sub>2</sub> gains (e.g., by reduced metamorphic gases or dissolution of uplifted, reduced continental sediments). The early environment was sufficiently reducing to scavenge O<sub>2</sub> (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<sub>2</sub> 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<sub>4</sub> by methanogenesis. When CH<sub>4</sub> is decomposed in the upper atmosphere by ultraviolet (UV) radiation, H escapes to space forever. The overall chemistry is CO<sub>2</sub> + 2H<sub>2</sub>O → CH<sub>4</sub> + 2O<sub>2</sub> → CO<sub>2</sub> + O<sub>2</sub> + 4H(↑ space), where the first reaction sums photosynthesis and methanogenesis. Currently, Earth gains oxygen by CH<sub>4</sub>-induced H escape at a negligible rate ~10<sup>10</sup> mol O<sub>2</sub> year<sup>-1</sup> because the rate depends on the magnitude of the atmospheric mixing ratio of CH<sub>4</sub> (*f*<sub>CH<sub>4</sub></sub>), which today is only 1.7 ppmv.

However, CH<sub>4</sub> would have been an important trace atmospheric constituent before the rise of O<sub>2</sub>. Today, the large biogenic flux of CH<sub>4</sub> to the atmosphere is oxidized, limiting *f*<sub>CH<sub>4</sub></sub> (9). But in the low-O<sub>2</sub> Archean, the kinetic fates of biogenic O<sub>2</sub> and CH<sub>4</sub> would have been reversed. O<sub>2</sub> would have been rapidly consumed and CH<sub>4</sub>, long-lived. Rapid reaction of O<sub>2</sub> with reduced metamorphic and volcanic gases and with upwelling oceanic cations like Fe<sup>2+</sup> would have buffered O<sub>2</sub> to trace levels (10). Also, organic carbon uplifted onto continents and washed to the ocean would have been consumed aerobically to produce CO<sub>2</sub> or anaerobically to make CH<sub>4</sub>

plus CO<sub>2</sub>, given that Archean elemental carbon is found in biologically mediated fine-grained shales (fixed from CO<sub>2</sub>) 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*<sub>CH<sub>4</sub></sub> ~200 to 3000 ppmv (16–18) if the biogenic CH<sub>4</sub> production rate were 0.1 to 1 times that of the present.

Abundant atmospheric CH<sub>4</sub> 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<sub>2</sub>) a few hundred to 1000 times larger than today has been postulated (20) but is improbable for several reasons. Paleosols indicate that pCO<sub>2</sub> 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<sub>2</sub> < 0.15 bar at 3.5 Ga (22). Abundant Archean marine limestone indicates calcite supersaturation then, as now (7). If pCO<sub>2</sub> were high, oceanic Ca<sup>2+</sup> should have been depleted, but evaporitic gypsum (23) suggests otherwise. Also, carbonatization of the seafloor should have lowered pCO<sub>2</sub> to levels inconsistent with a dominant greenhouse role (24). Further, Archean geochemical data do not indicate levels of acid weathering expected for pCO<sub>2</sub> > 100 times present (25). Consequently, the theory of Archean CH<sub>4</sub> greenhouse warming (Fig. 1A) has become favored (15–18, 21, 24). High CH<sub>4</sub> is consistent with relatively low pCO<sub>2</sub> because if a large greenhouse enhancement by CO<sub>2</sub> were added to warming dominated by CH<sub>4</sub>, CO<sub>2</sub> would be consumed in negative feedback by temperature-dependent weathering of continental silicates. A CH<sub>4</sub>-mediated climate can be stabilized in negative feedback with O<sub>2</sub>; e.g., increasing *f*<sub>CH<sub>4</sub></sub> causes greenhouse warming, which increases weathering, sedimentation, and, ultimately, organic burial rates. The latter, in turn, increases O<sub>2</sub>, which lowers *f*<sub>CH<sub>4</sub></sub>.

Climatologically important CH<sub>4</sub> (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*<sub>total</sub> (= *f*<sub>H<sub>2</sub>O</sub> + *f*<sub>H<sub>2</sub></sub> + 2*f*<sub>CH<sub>4</sub></sub> · · ·) (expressed as H<sub>2</sub> molecules for these calculations) determines the diffusion-limited H escape rate,  $\phi_{\text{escape}}$ , given by (27):

$$\phi_{\text{escape}} = 2.5 \times 10^{13} f_{\text{total}} (\text{H}_2 \text{ molecules cm}^{-2} \text{ s}^{-1}) \quad (1)$$

Today,  $\phi_{\text{escape}}$  is trivial (Table 1) because *f*<sub>total</sub> is small, given only 3 ppmv water vapor,

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## REPORTS

1.7 ppmv CH<sub>4</sub>, and 0.55 ppmv H<sub>2</sub> in the lower stratosphere. Upward transport of H in H<sub>2</sub>O, 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<sub>4</sub> is not cold trapped and increased H escape is unavoidable with increased  $f_{\text{CH}_4}$ . If Archean  $f_{\text{CH}_4}$  were  $\sim 1000$  ppmv (16–18),  $\phi_{\text{escape}}$  would be  $\sim 300$  times higher than today’s flux (Table 1). Large CH<sub>4</sub>-induced H escape

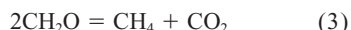
rates and significant global oxidation rates are general consequences of a high Archean  $f_{\text{CH}_4}$  (28).

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<sub>4</sub>-induced H escape in three cases: (i) when CH<sub>4</sub> originates from organic matter produced by oxygenic photosynthesis, (ii) when CH<sub>4</sub> derives from organic matter produced by anoxygenic autotrophic metabolisms, and (iii) when CH<sub>4</sub> derives from mantle H.

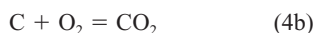
In (i), oxygen is gained irreversibly because photosynthetic splitting of water produces O<sub>2</sub> and H, and CH<sub>4</sub>-mediated escape removes the H forever. This process is schematically represented in Eqs. 2 through 5. Oxygenic photosynthesis can be summarized as



where CH<sub>2</sub>O represents organic matter. Production of CH<sub>4</sub> mainly derives from symbiotic communities of heterotrophs and methanogens that decompose organic matter (13).

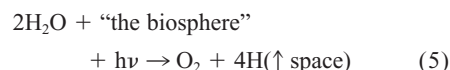


H escape to space via CH<sub>4</sub> can be represented as follows, noting that the detailed photochemistry (16) is rather more complex.



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

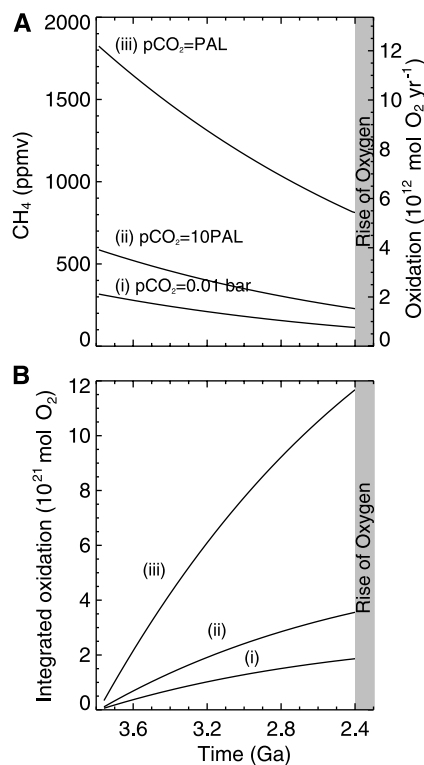
overall chemical transformation of the crustal system:



Consequently, the irreversible gain of oxygen from CH<sub>4</sub>-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<sub>2</sub> (e.g., via CH<sub>2</sub>O + H<sub>2</sub>O = 2H<sub>2</sub> + CO<sub>2</sub>) or CH<sub>4</sub> (via 2CH<sub>2</sub>O = CH<sub>4</sub> + CO<sub>2</sub>). During the Archean, if methanogens produced CH<sub>4</sub> by consuming metamorphic H<sub>2</sub>, or if CH<sub>4</sub> or H<sub>2</sub> fluxed directly from decomposed buried organic matter, the net effect of Eq. 5 would still apply.

Case (ii) concerns CH<sub>4</sub> originating from anoxygenic photoautotrophs or chemoautotrophs. Such prokaryotes use H<sub>2</sub>, reduced sulfur, or Fe<sup>2+</sup> as electron donors in biosynthesis (e.g., H<sub>2</sub>S + CO<sub>2</sub> + hν → CH<sub>2</sub>O + H<sub>2</sub>O + S). If CH<sub>4</sub> were derived from such organic matter, H escape would leave behind oxidized S or Fe, contributing to net crustal oxidation (though free O<sub>2</sub> is not produced), provided that the electron donor originated from the crust (e.g., metamorphic H<sub>2</sub>S). If the electron donor fluxed from the mantle, case (iii) would apply.

Case (iii) concerns methanogenic CH<sub>4</sub> 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-



**Fig. 1.** (A) The calculated mixing ratio of CH<sub>4</sub> (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<sub>4</sub> mixing ratios are calculated at three fixed levels of pCO<sub>2</sub> as indicated, where PAL indicates present atmospheric level  $\approx 0.0003$  bar. The upper pCO<sub>2</sub> limit, pCO<sub>2</sub> = 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<sub>4</sub>. The irreversible oxidation fluxes due to escape of hydrogen, corresponding to particular levels of CH<sub>4</sub>, are expressed as molar O<sub>2</sub> equivalents per year (right ordinate axis). We end calculations at 2.4 to 2.3 Ga, assuming that CH<sub>4</sub> levels collapsed upon the rise of atmospheric O<sub>2</sub>. (B) Integrated oxidation due to CH<sub>4</sub>-induced H escape to space, using the three atmospheric CH<sub>4</sub> levels from (A), shown with matching labels. Cumulative oxidation and the observed molar oxygen inventory in the continental crust (Table 2) are comparable.

**Table 1.** Earth’s oxygen fluxes.

Type of flux	Amount ( $\times 10^{12}$ mol O <sub>2</sub> year <sup>-1</sup> )	Action
Modern organic carbon burial flux*	10 ± 3	Production
Modern pyrite burial flux†	~1.7	Production
Modern Fe <sup>3+</sup> 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 to 1000 ppmv CH <sub>4</sub> §	0.7 to 7.0	Absolute gain

\*From (6). †FeS<sub>2</sub> is produced by bacteria that use sulfate and Fe<sup>3+</sup> as oxidants, with 15/8 moles of O<sub>2</sub> liberated per mole of sulfur (60). ‡The estimated net flux to the mantle is  $3.8 \times 10^{14}$  g Fe<sup>3+</sup> year<sup>-1</sup> (36). Fe<sup>3+</sup> derives from hydrothermal alteration of oceanic basalt; i.e.,  $22\text{FeO} + 2\text{SO}_4^{2-} + 4\text{H}^+ = \text{FeS}_2 + 7\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O}$ . Because 14 moles of Fe<sup>3+</sup> are subducted for 2 moles of SO<sub>4</sub><sup>2-</sup>, the net O<sub>2</sub> flux to the mantle is  $(3.8 \times 10^{14} \text{ g}/56 \text{ mol Fe}^{3+} \text{ year}^{-1})/14 = 0.5 \times 10^{12} \text{ mol O}_2 \text{ year}^{-1}$  if the SO<sub>4</sub><sup>2-</sup> had been derived from oxidation of SO<sub>2</sub> or  $1.9 \times 10^{12} \text{ mol O}_2 \text{ year}^{-1}$  if the SO<sub>4</sub><sup>2-</sup> had been derived from oxidation of H<sub>2</sub>S. §Calculated from Eq. 1.

## REPORTS

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  $f_{total} \approx 2f_{CH_4}$

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

Thus, if  $f_{CH_4}$  in the Archean atmosphere were  $\sim 100$  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.,  $\sim 1500$ -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
<i>Oxidized species</i>		
$O_2$ 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	$(3.1 \text{ to } 4.7) \times R_{AOS}$
Total $R_{Ox}$ (excluding oxygen transferred into carbonates)	2.0 to 2.9	$(1.5 \text{ to } 2.2) \times R_{redC}$
Net subducted $Fe^{3+}$ loss over 4 By§	2.0 to 7.6	$1.5 \text{ to } 5.8 \times R_{redC}$
Carbonate in the continental crust	2.2 to 7.1	
<i>Reduced species</i>		
Reduced carbon in the AOS system¶	0.56	
Reduced carbon in felsic intrusives, 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#	$\sim 1$	$\sim R_{redC}$

\*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  $\sim 1\%$  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<sub>2</sub>), 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<sup>3+</sup> 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 <sup>12</sup>C-enriched graphitic carbon relative to carbonate is unlikely because marine carbonates do not become increasingly <sup>12</sup>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<sub>4</sub>-induced H escape is chemically expected and can reconcile the observed redox inventory on its own. Other geochemical evidence of CH<sub>4</sub>-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<sub>2</sub>) 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<sub>2</sub> sources are apparent at 2.7 to 3.0 Ga from stromatolites (4). On the basis of δ<sup>15</sup>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<sub>2</sub> to rise. However, increased past volcanic outgassing would have also injected proportionately more CO<sub>2</sub>. Carbon isotopes from 3.5 Ga onward show that a roughly

constant fraction, *f*<sub>org</sub> (~20%) of the CO<sub>2</sub> flux into the biosphere was fixed biologically and buried as organic carbon with the remainder buried as carbonate (40). If *f*<sub>org</sub> were constant, increased outgassing in the past cannot, on its own, explain the oxic transition because as one goes back in time, O<sub>2</sub> production due to organic burial would have risen in parallel with O<sub>2</sub> losses. A second explanation of the rise of O<sub>2</sub> 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*<sub>org</sub> ~ 10 to >20%. Several uncertainties arise. First, during 3.5 to 2.9 Ga, *f*<sub>org</sub> 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<sub>2</sub> (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<sub>2</sub> at enhanced rates and canceling O<sub>2</sub> gains. A pulse of organic burial should merely cause atmospheric O<sub>2</sub> to rise and decay [like in the Paleozoic (50)], not accumulate irreversibly.

9. Today, the atmosphere receives ~3 × 10<sup>13</sup> mol CH<sub>4</sub> year<sup>-1</sup>, noting that much additional CH<sub>4</sub> 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<sub>4</sub> reached the atmosphere. Atmospheric oxidation rates of CH<sub>4</sub> are controlled by the initial step in the oxidation process that today takes ~7 to 12 years: OH + CH<sub>4</sub> = CH<sub>3</sub> + H<sub>2</sub>O. Oxidation becomes complete in the upper atmosphere, converting CH<sub>4</sub> into CO<sub>2</sub> and photodissociated fragments of water with the net reaction CH<sub>4</sub> + 2O<sub>2</sub> → CO<sub>2</sub> + 2H<sub>2</sub>O.
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<sub>2</sub> and CH<sub>2</sub>O via respiration and decomposition, fluxes of biogenic O<sub>2</sub> and CH<sub>4</sub> to the atmosphere are stoichiometrically balanced when photosynthesis and methanogenesis are combined (Eq. 2 × 2 + Eq. 3 results in CO<sub>2</sub> + 2H<sub>2</sub>O → CH<sub>4</sub> + 2O<sub>2</sub>). However, O<sub>2</sub> is much more reactive than CH<sub>4</sub>. Thus, in the weakly reducing Archean environment, O<sub>2</sub> would be lost rapidly to form soluble or insoluble oxides, whereas inert CH<sub>4</sub> would remain in the air at a much higher equilibrium concentration than today (16). O<sub>2</sub> would react rapidly with reduced gases (from volcanism, metamorphism, and diagenesis), upwelling ocean waters containing Fe<sup>2+</sup>, and riverine fluxes of dissolved reductants (e.g., organic complexes). A rough pO<sub>2</sub> can be estimated by assuming that only oxidation of oceanic Fe<sup>2+</sup> buffered O<sub>2</sub>, neglecting all other losses (to H<sub>2</sub>, CO, etc.). If Fe<sup>2+</sup> were ~3 ppm in the deep pre-oxic ocean (51), a mean oceanic upwelling rate of 5 m year<sup>-1</sup> gives a potential sink for O<sub>2</sub> of (3 × 10<sup>-6</sup>/56 mol cm<sup>3</sup>) × (5 × 10<sup>2</sup> cm year<sup>-1</sup>) × (3.6 × 10<sup>18</sup> cm<sup>2</sup>)/4 ~ 10<sup>13</sup> mol O<sub>2</sub> year<sup>-1</sup>, similar to modern organic burial rates. Thus, it is reasonable to estimate pO<sub>2</sub> by balancing Fe<sup>2+</sup> oxidation rates, φ<sub>ox</sub> (mol O<sub>2</sub> m<sup>-2</sup> year<sup>-1</sup>), with an assumed organic burial O<sub>2</sub> flux, F<sub>O<sub>2</sub></sub>, similar to modern values ~0.02 mol O<sub>2</sub> m<sup>-2</sup> year<sup>-1</sup>. Using φ<sub>ox</sub> ≈ 0.25ρ<sub>w</sub>H<sub>s</sub>k [OH<sup>-</sup>]<sup>2</sup> (pO<sub>2</sub>) [Fe<sup>2+</sup>] = F<sub>O<sub>2</sub></sub> (52) with rate constant k ≈ 5.3 ×

10<sup>17</sup> mol<sup>-2</sup> kg<sup>2</sup> atm<sup>-1</sup> year<sup>-1</sup>, seawater density ρ<sub>w</sub> = 1025 kg m<sup>-3</sup>, and mixed layer depth H<sub>s</sub> ~ 100 m, we deduce pO<sub>2</sub> ≤ 10<sup>-6</sup> bar for pH ≥ 7, consistent with paleosol constraints (2). The residence time of atmospheric O<sub>2</sub> would therefore have been approximately days. Archean CH<sub>4</sub> levels from photochemical models are ~1000 ppmv (16), yielding a residence time of (1.8 × 10<sup>20</sup> mol air × 10<sup>-3</sup>)/(3 × 10<sup>13</sup> mol CH<sub>4</sub> year<sup>-1</sup>) = 6000 years, using the present biogenic flux of CH<sub>4</sub> (9). This is the reverse of today, for which CH<sub>4</sub> has a residence time of 7 to 12 years (9) and O<sub>2</sub> cycles through the biosphere in ~6000 years (53).

11. H. D. Holland, in (7), p. 353.
12. The presence of CH<sub>4</sub>-generating archaeobacteria (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<sub>4</sub> 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<sub>2</sub> or SO<sub>4</sub><sup>2-</sup>—are globally indicated in the late Archean by organic carbon isotopes (13–15). Methanogens fractionate the stable isotopes of carbon (<sup>13</sup>C and <sup>12</sup>C) in favor of <sup>12</sup>C. When methanogen CH<sub>4</sub> is consumed by methanotrophs, the carbon is further fractionated, leading to organic carbon much depleted in <sup>13</sup>C. At ~2.7 to 2.8 Ga, methanotrophic organic δ<sup>13</sup>C implies >20 ppmv CH<sub>4</sub> (13, 15). CH<sub>4</sub> 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<sub>2</sub> or SO<sub>4</sub><sup>2-</sup>. 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<sup>+</sup> → H<sup>+</sup> + 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<sub>2</sub>, O, O<sub>2</sub>, H, and He) absorb UV radiation and warm the thermosphere. The Archean's lack of O<sub>2</sub> 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<sub>2</sub> based on detailed calculations of the thermospheric temperature for an anoxic Earth (55). Greater pCO<sub>2</sub> could cool the thermosphere radiatively. The mesopause (the cold base of the thermosphere at about ~85-km altitude, where CO<sub>2</sub> cools radiatively) occurs at a pressure level inversely proportional to f<sub>CO<sub>2</sub></sub><sup>0.5</sup>, where f<sub>CO<sub>2</sub></sub> is the mixing ratio of CO<sub>2</sub> (56). At the upper pCO<sub>2</sub> 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<sub>2</sub> abundances and prevent significant thermospheric cooling. The radiative cooling effects of molecular CH<sub>4</sub> on the thermopause can be neglected because CH<sub>4</sub> 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.

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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<sub>2</sub>, 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<sub>2</sub> 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 [<sup>2</sup>D/<sup>1</sup>H (standard)]] for standard mean ocean water (SMOW), expressed in parts per thousand. δD = {[(<sup>2</sup>D/<sup>1</sup>H (sample) - <sup>2</sup>D/<sup>1</sup>H (standard))]/(<sup>2</sup>D/<sup>1</sup>H (standard))} × 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 δD = -150 to -300‰. If oxygenic photosynthesis coupled to CH<sub>4</sub>-induced H escape caused cumulative oxidation ~2.5 × 10<sup>21</sup> mol O<sub>2</sub> (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 manifesta-

tion 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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