

UNDERSTANDING THE EVOLUTION OF ATMOSPHERIC REDOX STATE FROM THE ARCHAEOAN TO THE PROTEROZOIC. David C. Catling¹, Mark W. Claire², Kevin J. Zahnle³ University of Washington, Astrobiology Program, Box 351640, Seattle, WA 98195, USA. (E-mail davidc@atmos.washington.edu), ²University of Washington, Box 351580, Seattle, WA 98195, USA. ³MS 245-3, Space Science Division, NASA Ames Research Center, Moffett Field, CA 94035, USA.

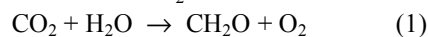
Introduction: Geological differences between the ancient and modern Earth show that there was too little O₂ in the early atmosphere to leave traces of oxidation that today are common, such as the reddening of exposed iron-rich rocks [1]. The onset of oxidized paleosols, red beds, and the ensuing absence of detrital pyrite, siderite and uraninite all indicate an increase in atmospheric O₂ levels at 2.4-2.3 Ga. Recently, measurements of mass-independently fractionated sulfur isotopes have confirmed the timing of the oxic transition [2]. The fossil record arguably shows that this Palaeoproterozoic oxic transition changed the course of evolution. The oldest macroscopic fossils of possible eukaryotic origin occur in 1.8 Ga rocks [3], 4-5 mm long possibly multicellular fossils appear at 1.7 Ga [4], and acritarchs significantly increase in abundance after 1.7 Ga. However, the cause of the oxic transition remains poorly understood because determining how and why the O₂ increase occurred requires an integrated grasp of the redox behaviour of the atmosphere, ocean, biosphere and lithosphere.

An important conundrum: Oxygenic photosynthesis is the only plausible source of free O₂ that could have caused the oxic transition [5]. However, the oxic transition occurred at ~2.4-2.3 Ga [1,2,6] whereas cyanobacterial oxygenic photosynthesizers existed in the oceans long before that. Isotopic fractionation of carbon between sedimentary organic carbon and carbonates is about 30‰ back to 3.5 Ga and characteristic of photosynthetic fractionation, which suggests an early origin for oxygenic photosynthesis, but is not, on its own, conclusive [7]. What is conclusive is that hydrocarbon biomarkers derived from oxygenic photosynthetic cyanobacteria and from eukaryotic sterols are found at 2.7 Ga [8]. Also localized biological oxygen sources are apparent from 2.7-3.0 Ga [9,10]. This evidence presents a puzzle, given the oft-stated (but perhaps naive) opinion that the rise of O₂ could be explained if the rise coincided with the origin of oxygenic photosynthesis.

Explanations for the rise of O₂: Several ideas have been put forward to account for how oxygenic photosynthesis could have originated long before a detectable rise of O₂. One explanation is that large positive carbonate isotope excursions from 2.4-2.1 Ga were due to a massive

pulse of organic burial that caused the rise of O₂ [11]. However, given the geologically short residence time of O₂ (~2-3 million years, even today), a pulse of organic burial would merely cause a parallel pulse in O₂. Atmospheric O₂ would return to its previous low levels once burial and oxidation of previously buried carbon had re-equilibrated. For O₂ to remain in the atmosphere, a secular shift in source and sink fluxes of O₂ must occur that forces a higher O₂ equilibrium level. A second hypothesis attempts to take account of this issue by suggesting that as geothermal heat declined due to the decay of radioactive materials inside the Earth, the flux of volcanic gases dwindled, lessening the sink on O₂. However, increased past volcanic outgassing would have also injected proportionately more CO₂. Carbon isotopes from 3.5 Ga onwards show that roughly ~20% of the CO₂ flux into the biosphere was fixed biologically and buried as organic carbon with the remainder buried as carbonate [7]. Consequently, increased outgassing in the past, on its own, cannot explain the oxic transition because going back in time, O₂ production due to organic burial would have risen in parallel with O₂ losses. A third explanation of the rise of O₂ takes account of the problem with the previous idea and invokes a gradual, irreversible shift of volcanic gases from reduced to oxidized [12,13]. However, studies of redox-sensitive Cr and V abundance in igneous rocks show that the mantle's oxidation state (i.e., oxygen fugacity), which controls the redox state of volcanic gases, only permits an increase in H₂ relative to CO₂ by a factor ≤1.8, which cannot account for a sufficient change in the sink on O₂ [14,15].

Atmospheric flip states: Excess hydrogen-bearing species vs. excess oxygen: On a geologic timescale, a decrease by a factor of ~3 in the H₂/CO₂ ratio of volatile fluxes is sufficient to flip the atmosphere from a redox state by hydrogen-bearing species like CH₄ to an O₂-rich state. This can be understood as follows. Carbon isotopes imply that the ratio of the burial flux of organic carbon to the total flux of carbon input has been ~1:5 since about 3.5 Ga [7]. In photosynthesis, one mole of buried organic carbon generates one mole of O₂:



where "CH₂O" represents organic matter. The organic carbon has to be buried in sediments be-

cause otherwise respiration or decay reverse eq. (1). Thus the ratio F_B/F_{CO_2} of the O_2 flux (F_B) produced by organic burial to the carbon outgassing flux (dominated by CO_2) is about 1/5. Today, volatile reducing fluxes from the Earth (F_{H_2}), which are mostly hydrogen, consume $\sim 1/3$ of the flux of O_2 , F_B [16,17]. We can define an oxygenation parameter, K , such that

$$\left(\frac{F_B}{F_{CO_2}}\right)\left(\frac{F_{CO_2}}{F_{H_2}}\right) = \left(\frac{F_B}{F_{H_2}}\right) = K \quad (2)$$

Because removal of O_2 by gas reactions is rapid, when $K < 1$, the atmosphere has very low O_2 ; when $K > 1$, the atmosphere is O_2 rich. Today $K \sim 3$ (i.e., the flux of hydrogen, expressed in terms of moles of O_2 it consumes, is about 1/3 of the net O_2 flux). As a consequence, O_2 reaches a high concentration in today's atmosphere and the production associated with organic burial is mostly balanced by loss to oxidative weathering. Typical estimates for modern fluxes are $F_{CO_2} \sim 50 \times 10^{13}$ mol C yr⁻¹ [18], $F_B \sim 10^{13}$ mol O_2 yr⁻¹, and $F_{H_2} \sim 0.3 \times 10^{13}$ mol O_2 consumption yr⁻¹ [16,17]. Clearly, if the ratio F_B/F_{CO_2} has been $\sim 1/5$ since 3.5 Ga by isotopic constraints, then the variable in eqn. (2) that can change K is F_{CO_2}/F_{H_2} . If in the past $K < 1$, the atmosphere would have been redox-dominated by excess hydrogen-rich species even if organic burial and associated O_2 production were the same as today. To obtain $K < 1$ requires a decrease in F_{CO_2}/F_{H_2} by a factor of ~ 3 or more compared to today.

The importance of biogenic methane and the escape of hydrogen to space: We have argued in previous work that a shift in the redox state of volcanic gases combined with metamorphic gases most likely accounted for sufficient oxidation of gases emanating from the solid Earth to effect the oxic transition [19], before 2.4 Ga, excess reductants rapidly scavenged O_2 and the excess hydrogen flux set the atmosphere in a redox state dominated by hydrogen-rich species, such as CH_4 (i.e., $K < 1$). In this hypothesis, gradual oxidation of the Earth and its outgassing fluxes (i.e., the increase in F_{CO_2}/F_{H_2}) is ultimately driven by the escape of hydrogen to space. When hydrogen escapes from Earth into space, the planet as a whole is irreversibly oxidized. When hydrogen originates from the crust (or mantle), and escapes to space, the crust (or mantle) is irreversibly oxidized. The metamorphic recycling of more reduced Archaean crust would have produced more reducing volatiles than the recycling of today's more oxidized crust, as a matter of redox conservation. That the early crust was more reduced than today is suggested by excess reduced minerals in the Archaean.

To complete our picture of the early atmosphere we must consider the role of biology. Methane is an unavoidable product of microbial degradation of organic detritus. It has been argued that the advent of oxygenic photosynthesis would have supplied vastly more organic substrate compared to the world before oxygenic photosynthesis [20]. Consequently, it is reasonable to suggest that abundant CH_4 would have resulted from the advent of oxygenic photosynthesis (due to more organic substrate) rather than increased O_2 , which we might naively expect. Methane is more likely to win control of the redox state of the atmosphere because CH_4 is basically inert— it reacts only with O_2 (via photochemical intermediates) and oxygen's derived products such as sulfate— whereas O_2 reacts with a multitude of chemical species such as Fe^{2+} , sulfides, and geothermal gases (H_2 , CO , etc.). Of course, most biogenic O_2 is rapidly consumed in a closed loop of aerobic respiration that does not make net O_2 . For the remaining fixed carbon, the methane production rate will always likely exceed the slow flux of organic carbon burial. CH_4 and O_2 are thus emitted to the atmosphere in virtual stoichiometric balance through the coupling of photosynthesis and methanogenesis described by $CO_2 + 2H_2O = CH_4 + 2O_2$. To first order, CH_4 and O_2 mutually annihilate via the reverse reaction. However, a little CH_4 is left over because O_2 reacts with abundant reduced chemicals in the Archaean environment whereas CH_4 does not. Photochemical models show that CH_4 would accumulate to 10^2 - 10^3 parts per million by volume (ppmv), with the excess flux of CH_4 balanced by photolytic destruction in the upper atmosphere. Such abundant CH_4 provides enough greenhouse warming to counteract the faint young sun [21]. However, large amounts of CH_4 inevitably cause a large rate of hydrogen escape to space. For example, at ~ 300 ppmv CH_4 , hydrogen loss causes an oxidation rate $\sim 1/3$ of the current rate at which O_2 is consumed by weathering. But unlike weathering, oxidation by H escape is unbalanced by accumulation of reductants elsewhere on Earth. In a nutshell, a CH_4 greenhouse must irreversibly oxidize the Earth.

An idealized biogeochemical model: To demonstrate the conceptual essence of how our scenario for the oxic transition works, we have constructed a biogeochemical redox model. In this model, the rate of change of the number of Tmol of O_2 in the atmosphere, $[O_2]$, is calculated by solving the following eqn.:

$$\frac{d[O_2]}{dt} = F_{\text{source}} - F_{\text{sink}} \quad (3)$$

Here F_{sink} is the removal flux of O_2 from the atmosphere (in Tmol O_2 yr⁻¹) due to oxidation reac-

tions, F_{source} is the source of O_2 (in Tmol yr^{-1}), and t is time. O_2 and CH_4 concentrations are calculated by expanding (1):

$$\frac{d[\text{O}_2]}{dt} = 2F_{\text{CH}_4} + F_{\text{B}} - 2k_{\text{eff}}[\text{O}_2][\text{CH}_4] - k_e[\text{CH}_4] - F_{\text{M}} - F_{\text{W}} \quad (4)$$

$$\frac{d[\text{CH}_4]}{dt} = F_{\text{CH}_4} - k_{\text{eff}}[\text{O}_2][\text{CH}_4] - k_e[\text{CH}_4] \quad (5)$$

Here we assume that O_2 and CH_4 are stoichiometrically balanced in biogenic production via $\text{H}_2\text{O} + \text{CO}_2 = \text{CH}_4 + 2\text{O}_2$, as described earlier. The model uses an effective rate constant, k_{eff} (dependent on $[\text{O}_2]$ and the ozone layer, derived from photochemical models) for the net reaction between O_2 and CH_4 in the troposphere. Here k_e is a constant for hydrogen escape that accounts for the photolytic destruction of CH_4 limited by the diffusion of hydrogen through the upper atmosphere. The small leak of organic carbon F_{B} to sediments contributes to F_{source} . The removal flux of O_2 , F_{sink} , is due to the reaction of O_2 with reduced volcanic gases and reduced metamorphic gases (lumped together as F_{M}), and the weathering reduced material on the continents (F_{W}).

Model results: Timing: We find that the oxic transition occurs when F_{M} drops below F_{B} , as predicted by eq. (2) with $F_{\text{H}_2} = F_{\text{M}}$. Essentially, geological fluxes of reducing volatiles and their rate of decrease set the timing of the oxic transition. **Nonlinear oxic transition:** At low CH_4 , the only loss of CH_4 is oxidation and $k_{\text{eff}}[\text{O}_2][\text{CH}_4] \approx$ constant. However, k_{eff} depends on $[\text{O}_2]$ and decreases with a thicker ozone layer. This causes O_2 to rise relatively sharply because O_2 losses decrease as O_2 increases, i.e., a positive feedback is produced.

Future work: Our model is a useful tool, but is highly simplified because important aspects of the Earth are yet to be included. Such additions include climatic feedbacks on the biosphere (limiting early CH_4), the details of how temperature structure bears on photochemistry, the sulfur cycle, and a more complex biosphere. However, the basic overall result – an oxic transition accompanied by a decrease of methane—remains a robust prediction, given the overall character of the equations and unidirectional hydrogen escape.

References: [1] Holland, H. D. (1999) *Geochem. News*, 100, 20-22. [2] Farquhar, J. et al. (2000) *Science* 289, 756-758 (2000). [3] Han, T.-M. & Runnegar B. (1992) *Science* 257, 232-35. [4] Shixing, Z. & Huineng, C. (1995) *Science* 270, 620-622. [5] Walker, J. C. G. (1977) *Evolution of the Atmosphere* (Macmillan, New York) [6] Cloud, P. (1968) *Science* 160, 729-36. [7] Schidlowski, M. (1988) *Nature* 333, 313-18. [8] Brocks, J. J. et al. (1999) *Science* 285, 1033-36. [9] Beukes, N. J. & Lowe, D. R. (1989) *Sedimentology* 36, 383-97. [10] Buick, R. (1992) *Science* 255, 74-77. [11] Karhu, J. A. & Holland, H. D. (1996) *Geology*, 24, 867-70. [12] Kasting, J. F. et al. (1993) *J. Geol.* 101, 245-25. [13] Kump L. R. et al. (2001) *G³* [14] Delano J. W. (2001) *Origins Life Evol. Biosphere* 31, 311-41. [15] Canil, D. (2002) *Earth Planet. Sci. Lett.* 195, 75-90. [16] Holland, H. D. (1978) *The Chemistry of the Atmosphere and Oceans* (Wiley, New York). [17] Holland, H. D. (2002) *GCA* 66, 3811-26 [18] Sleep, N. H. & Zahnle, K. J. (2000) *JGR* 106, 1373-99. [19] Catling et al. (2001) *Science*, 293, 839-43. [20] Des Marais (2000) *Science* 289, 1703. [21] Pavlov et al. (2000) *JGR* 105, 11981-90.

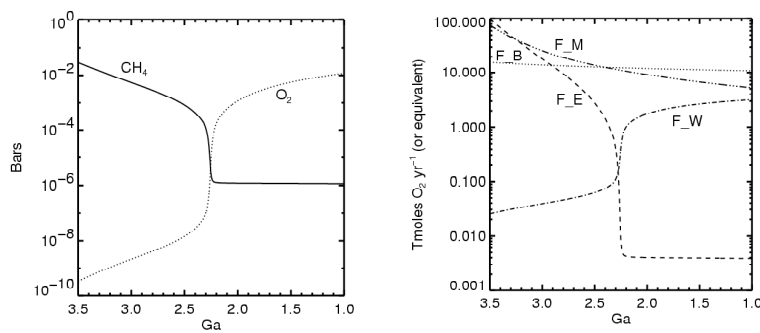


Fig.1: Result of a conceptual redox flux box model. **Left:** Atmospheric gases as a function of time. **Right:** Fluxes in the model in Tmol yr^{-1} of consumption/production of O_2 equivalents. (1 $\text{Tmol} = 10^{12}$ mol).