

**UNDERSTANDING THE EVOLUTION OF ATMOSPHERIC REDOX STATE FROM THE ARCHAEOAN TO THE PROTEROZOIC.** David C. Catling<sup>1</sup>, Mark W. Claire<sup>2</sup>, Kevin J. Zahnle<sup>3</sup>.

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**Introduction:** Geological differences between the ancient and modern Earth show that there was too little O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub> could be explained if the rise coincided with the origin of oxygenic photosynthesis.

**Explanations for the rise of O<sub>2</sub>:** Several ideas have been put forward to account for how oxygenic photosynthesis could have originated long before a detectable rise of O<sub>2</sub>. 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 O<sub>2</sub> [11]. However, given the geologically short residence time of O<sub>2</sub> (~2-3 million years, even today) a pulse of organic burial would merely cause a parallel pulse in atmospheric O<sub>2</sub>. Atmospheric O<sub>2</sub> would return to its previous low levels once burial and oxidation of previously buried carbon had re-equilibrated. For high O<sub>2</sub> to persist, a secular shift in source and sink fluxes of O<sub>2</sub> must occur that forces a higher O<sub>2</sub> 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 O<sub>2</sub>. However, increased past volcanic outgassing would have also injected proportionately more CO<sub>2</sub>. Carbon isotopes from 3.5 Ga onwards show that roughly ~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 [7]. Consequently, increased outgassing in the past, on its own, cannot explain the oxic transition because going back in time, O<sub>2</sub> production due to organic burial would have risen in parallel with O<sub>2</sub> losses. A third explanation of the rise of O<sub>2</sub> 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 H<sub>2</sub> relative to CO<sub>2</sub> by a factor of ~1.8, which cannot account for a sufficient change in the sink on O<sub>2</sub> [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 H<sub>2</sub>/CO<sub>2</sub> ratio of fluxes is sufficient to flip the atmosphere from a redox state dominated by hydrogen-bearing species like CH<sub>4</sub> to an O<sub>2</sub>-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 O<sub>2</sub>:



where "CH<sub>2</sub>O" represents organic matter. The organic carbon has to be buried in sediments be-

cause otherwise respiration or decay reverses eq. (1). Thus the ratio  $F_B/F_{CO_2}$  of the  $O_2$  flux ( $F_B$ ) produced by organic burial to the total carbon input flux (dominated by  $CO_2$ , including its dissolved product,  $HCO_3^-$ , from weathering) 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

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

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  $O_2$  production associated with organic burial is mostly balanced by loss to oxidative weathering. Typical estimates for modern fluxes are  $F_B \sim 10^{13}$  mol  $O_2$  yr $^{-1}$  and  $F_{H_2} \sim 0.3 \times 10^{13}$  mol  $O_2$  consumption yr $^{-1}$  [16,17].  $F_{CO_2}$  must be  $\sim 5 \times 10^{13}$  mol C yr $^{-1}$  for carbon isotopic balance, although accounting for all components of this flux is difficult [18]. 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 eq. (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  $\sim 3$  or more compared to today.

**The importance of biogenic methane and the escape of hydrogen to space:** We have argued in previous work that gases emanating from the solid Earth must have become more oxidized with time to account for the oxic transition [19]. Here we took the gases to include volcanic and metamorphic sources. Before 2.4 Ga, excess reductants rapidly scavenged  $O_2$  and the excess hydrogen flux enabled the atmosphere to be 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  $F_{CO_2}/F_{H_2}$  with time) is ultimately driven by the escape of hydrogen to space. By definition, the chemical process of reduction is when hydrogen is chemically added to a body; conversely, if hydrogen is removed from compounds within a body, the body is oxidized. Thus, 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 Archaean rocks.

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  $\sim 300$  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 eq.:

$$\frac{d[\text{O}_2]}{dt} = F_{\text{source}} - F_{\text{sink}} \quad (3)$$

Here  $F_{\text{sink}}$  is the removal flux of  $\text{O}_2$  from the atmosphere (in  $\text{Tmol O}_2 \text{ yr}^{-1}$ ) due to oxidation reactions,  $F_{\text{source}}$  is the source of  $\text{O}_2$  (in  $\text{Tmol yr}^{-1}$ ), and  $t$  is time.  $\text{O}_2$  and  $\text{CH}_4$  concentrations are calculated by expanding (3):

$$\frac{d[\text{O}_2]}{dt} = 2F_{\text{CH}_4} + F_{\text{B}} \quad (4)$$

$$-2k_{\text{eff}}[\text{O}_2][\text{CH}_4] - k_e[\text{CH}_4] - F_{\text{M}} - F_{\text{W}}$$

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

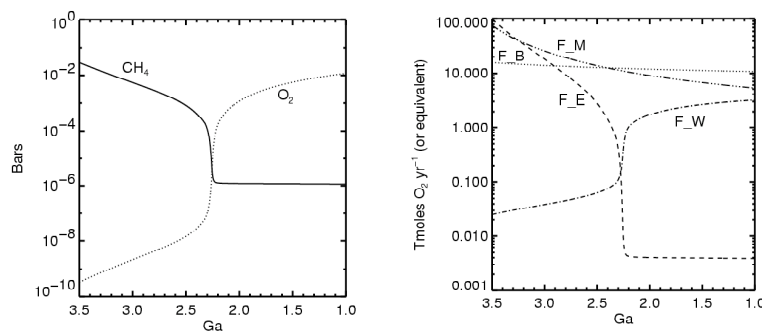
Here we assume that  $\text{O}_2$  and  $\text{CH}_4$  are stoichiometrically balanced in biogenic production via  $\text{H}_2\text{O} + \text{CO}_2 = \text{CH}_4 + 2\text{O}_2$ , as described earlier. The model uses an effective rate constant,  $k_{\text{eff}}$  derived from photochemical models (dependent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

**Model results: Timing:** We find that the oxic transition occurs when  $F_{\text{M}}$  drops below  $F_{\text{B}}$ , 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  $\text{CH}_4$ , the only loss of  $\text{CH}_4$  is oxidation and  $k_{\text{eff}}[\text{O}_2][\text{CH}_4] \approx$  constant. However,  $k_{\text{eff}}$  depends on  $[\text{O}_2]$  and decreases with a thicker ozone layer. This causes  $\text{O}_2$  to rise relatively sharply because  $\text{O}_2$  losses de-

crease as  $\text{O}_2$  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  $\text{CH}_4$ ), 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.

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**Fig.1:** Result of a conceptual redox flux box model. **Left:** Atmospheric gases as a function of time. **Right:** Fluxes in the model in  $\text{Tmol yr}^{-1}$  of consumption/production of  $\text{O}_2$  equivalents. (1  $\text{Tmol} = 10^{12}$  mol).