The Great Oxidation Event (GOE): Biogeochemical Feedback and Tipping Points

Andrew P. Ingersoll
Division of Geological and Planetary Sciences
California Institute of Technology
Pasadena, CA 91125
api@caltech.edu

The Great Oxidation Event (GOE): Biogeochemical Feedback and Tipping Points

Andrew P. Ingersoll
Division of Geological and Planetary Sciences
California Institute of Technology
Pasadena, CA 91125
api@caltech.edu

Submitted January 7, 2024

Abstract

Approximately 1.4 Ga after life first appeared, atmospheric O_2 suddenly jumped by more than an order of magnitude over a 20-50 Ma period. The contrast between these two timescales does not seem to be due to any sudden, large-amplitude change in external forcing. However, it could be due to processes intrinsic to the geobiological system itself, namely, positive feedback between atmospheric O_2 and photosynthetic bacteria: More O_2 leads to more photosynthesis, which leads to more O_2, and so on. The key to this feedback is the 15-fold greater efficiency of aerobic vs anaerobic respiration and the tight coupling of respiration and photosynthesis inside the cell. As in the climate system, feedback leads to tipping points, where a rapid, large-amplitude change in the state of the system occurs. Examples include transitions to a snowball Earth and/or a runaway greenhouse. For the geobiological system, the GOE is the tipping point, and the long, slow buildup before the GOE is the gradual oxidation of Earth's surface and ocean, either due to burial of organic matter, oxidation of volcanic gases, and/or escape of hydrogen to space. The feedback hypothesis is offered as a framework for interpreting observations leading up to and during the GOE.

The most precise timing of the GOE comes from the isotopes of sulfur (Farquhar et al., 2000) in sedimentary rocks. Observations place the event 2.33 Ga ago, 1.4 Ga after life first appeared, and its duration at $\leq$ 30 Ma (Luo et al., 2016). The time span of the duration is limited by the precision of the observations and may be just an upper bound. Evidence for the GOE is that departures of the isotopes of sulfur from a global standard suddenly started following a linear relation with respect to mass. The measurement (Farquhar et al., 2011) is illustrated in the Supplementary Information. The interpretation is that instead of appearing in a variety of valence states, as happens for gases in the atmosphere, most of the sulfur around the globe was suddenly oxidized to sulfate, SO_4^{2-}, which led to mass-dependent fractionation.

There are two fundamental questions: What caused the long (1.4 Ga) delay in the appearance of O_2 after life first appeared? And why did the delay end so abruptly? The delay is often attributed to reduced gases like H_2S, SO_2, CH_4 and H_2, which are emitted by volcanoes (Cadle, 1980) and would tend to maintain anoxic conditions at the surface, *i.e.,* in the crust, atmosphere and oceans. Yet the earliest life forms of life, the cyanobacteria, are capable of photosynthesis even under anoxic conditions. Subduction of the resulting organic matter into the mantle could have led to a separation of carbon into reduced forms like graphite and diamond and oxidized forms like carbonate and CO_2. The oxidized forms could feed into the mixture of volcanic gases and would tend to oxidize the surface. Escape of hydrogen to space would also oxidize the surface. Eventually the ocean and atmosphere would cross the threshold from anaerobic to aerobic metabolism. Then photosynthesis would have become 15 times more efficient, which is a positive feedback – the more oxygen is in the atmosphere, the more rapidly the bacteria produce oxygen. That threshold is the GOE. It is a tipping point – an abrupt change in the state of a system – and would have taken place on a short, biological time scale, although having a variety of niches could have spread the timescale far enough to be resolved in the sedimentary record.

The US Geological Survey's upper limit for anoxic water has a partial pressure of 1.2 mbar at equilibrium, corresponding at 25 C° to a solution with 0.5 mg L^{-1} of dissolved O_2 (Wikipedia entries: Henry's Law and Anoxic Waters). This upper limit is also known as the Pasteur point, where microorganisms adapt from fermentation to aerobic respiration. However, atmospheric O_2 before the GOE is controversial. Some studies show that O_2 was widespread and pervasive in microaerobic marine environments hundreds of Ma before the GOE (Waldbauer et al., 2011). But other studies show that the cited evidence, e.g., trace metal oxidation of sediments, including sulfur, might be due to oxidative weathering after the GOE (Slotznick et al., 2022). If so, then oxygenic photosynthesis would have appeared shortly before the rise of oxygen, not hundreds of millions of years before it (Ward et al., 2016). Furthermore, studies of the genome of cyanobacteria, which are the only bacteria capable of oxygenic photosynthesis, suggest that they arrived late (Battistuzzi et al., 2004). Some suggest that the GOE was directly caused by the evolution of cyanobacteria (Soo et al., 2017). In that view, oxygenic photosynthesis was a mutation waiting to happen. Bacteria may have tried it out many times before the slow oxidation of the surface made it viable.

The 1.4 Ga build-up followed by a short ($\leq$ 30 Ma), large-amplitude transition, resembles the effects of feedback in the climate system. Positive feedback occurs when the output of a system amplifies the input. An example is ice-albedo feedback (Budyko, 1969). The input is the incident sunlight, and the output is the Earth's surface temperature. The positive feedback is the increase in the fraction of sunlight reflected back to space as the Earth gets colder. A cold Earth has more snow and ice, which reflect more sunlight, making the Earth even colder. At the same time, there is negative feedback, the effect of infrared radiation, which tends to bring the Earth into equilibrium with the absorbed sunlight. Fig. 1 shows how this works. There are two equilibrium states, a warm Earth and a snowball Earth. If the incident sunlight were decreasing, the warm Earth would reach the tipping point on the left and drop to a snowball state. If the incident sunlight were increasing and the Earth were in the snowball state, it would reach the tipping point on the right and jump up to the warm Earth state. Water vapor feedback is another example. This is where the Earth gets warmer and has more water vapor in the atmosphere, which traps more heat since water is a potent greenhouse gas. If the incident sunlight continued to increase, the Earth's liquid ocean would become a supercritical water vapor atmosphere. The tipping point for a runaway greenhouse may lie between the orbits of Earth and Venus (Ingersoll, 1969).

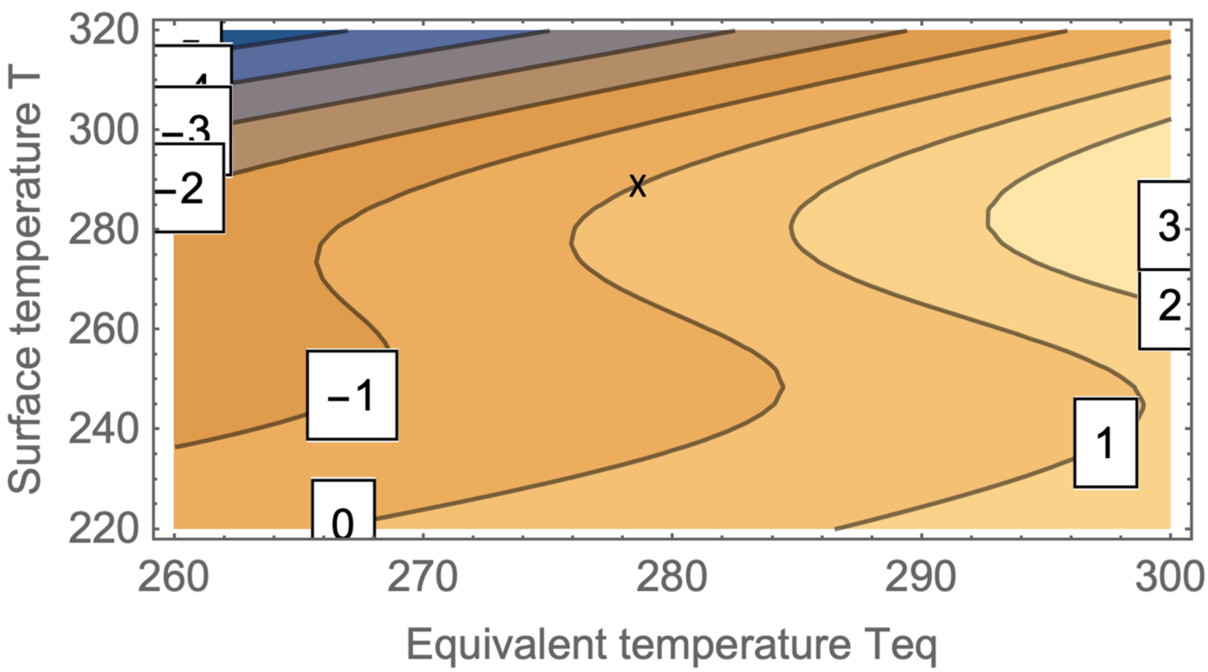

Fig. 1: Rate of change dT/dt (the contours) as a function of surface temperature T (y-axis) and solar forcing T*eq* (x-axis), the latter being the temperature of a perfectly absorbing, black isothermal sphere in equilibrium with sunlight. The units of dT/dt depend on the size of the thermal reservoir and are arbitrary in this figure. The feedback is the visual albedo, which decreases from 0.72 at low T to 0.22 at high T. Positive contours are where dT/dt > 0, and negative contours are where dT/dt < 0. The zero contour shows the equilibrium solutions, where T is not changing, and they group into three parts defined by the slope. Near the upper and lower parts, dT/dt is toward the zero contour, indicating that those parts are stable. Near the middle part, dT/dt is away from the zero contour - positive above it and negative below it, indicating that that part is unstable. The left and right extrema of the zero contour are the tipping points, and they define the places where the system can jump from one stable equilibrium to the other. The X at the center denotes the present

Earth according to this model. See Supplementary Information for the mathematical formulation.

In the geobiological system, positive feedback would occur if more atmospheric oxygen led to more oxygenic photosynthesis by cyanobacteria, which led to more atmospheric oxygen, and so on. The feedback proposed here is intrinsic to cyanobacteria. It arises because the efficiency of oxygenic photosynthesis is strongly coupled to the efficiency of respiration, which is a strongly increasing function of atmospheric O_2. All organisms, both autotrophs, which make glucose, and heterotrophs, which only consume it, live by harnessing the chemical energy of glucose and oxygen, that is, by breathing. The glucose is made during photosynthesis, which is the opposite of respiration. Aerobic respiration breaks glucose down to CO_2 and H_2O. It requires direct access to O_2 and is ~15 times more efficient in harnessing the chemical energy than anaerobic respiration (Flurkey, 2010), which uses the fact that glucose is an unstable molecule that is protected by a kinetic barrier. Anaerobic respiration produces lactic acid and ethanol by fermentation (Stal and Moezelaar, 1997), yielding 2 ATP molecules compared with ~30 from aerobic respiration.

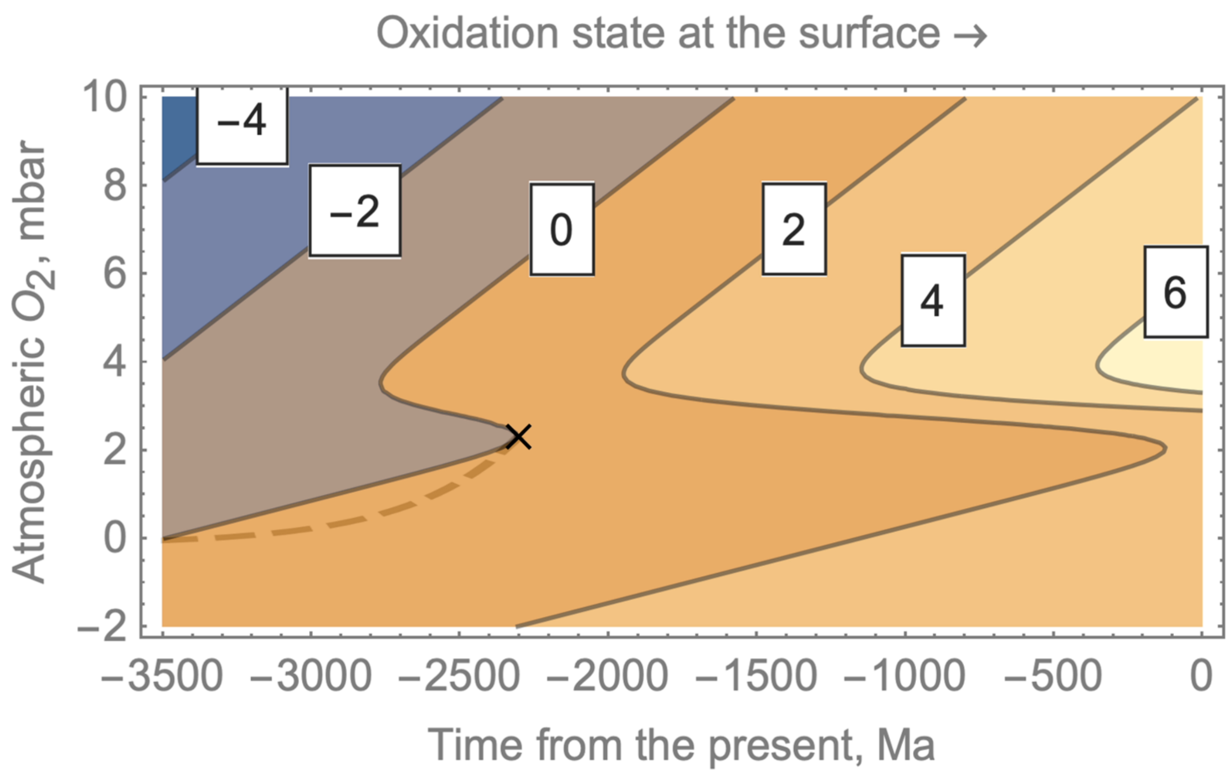

Fig. 2: Rate of change of atmospheric O_2 (the units of the contours are arbitrary) as a function of atmospheric O_2 (y-axis, units are mbar) and time (x-axis, Ma). The oxidation state of Earth's crust is the input variable, and it is increasing on a Ga time scale. The × marks the start of the GOE and is analogous to the right-hand tipping point of Fig. 1. The dashed line is one of the alternate series of equilibrium states leading up to the GOE.

In cyanobacteria, respiration and photosynthesis are tightly coupled. They share the same metabolic pathway, the thylakoid membrane, for electron transfer (Kirchhoff, 2014). The molecule that carries the electrons, plastoquinone, functions as a redox sensor that drives the magnitude and direction of the transfer to maintain metabolic and redox homeostasis (Havaux, 2020; Shimakawa et al., 2021). Respiration supplies metabolic energy to the cell during the night, and it protects the cell from excess oxygen during the day. The close relationship also occurs in mm-thick mats and films, where the embedded heterotrophs provide respiration that enables photosynthesis by the cyanobacteria (Kuhl et al., 1996; Ploug, 2008; Staal et al., 2003). Finally, the fact that about half of global primary production is used for respiration by the photoautotrophs, and the other half goes out to feed the heterotrophs (Field et al., 1998), is evidence that photosynthesis and respiration are coupled on a global scale as well (Paumann et al., 2005).

Searching the Web of Science on the three keywords (cyanobacteria, photosynthesis respiration) produces 526 articles. The origins of photosynthesis and respiration have been widely studied (Schopf, 2014; Soo et al., 2017). Adding a fourth keyword (feedback) reduces the number to 9. Most of the 9 articles are about eukaryotes. Some are about specific strains of cyanobacteria. The one that uses the tight coupling of respiration and photosynthesis does so in the context of endosymbiotic events and massive gene transfer to eukaryotic host cells (Falkowski and Godfrey, 2008). A different kind of feedback involves atmospheric O_2 leading to an ozone layer that blocks harmful UV radiation (Goldblatt et al., 2006). Then cyanobacteria flourished according to this hypothesis. Other parts of the Earth system may add their own feedbacks, but they are not discussed in this paper.

Fig. 2 is a conceptual model of the GOE. It captures the idea of atmospheric oxygen reaching a tipping point due to the slow increase in the oxidation state of the atmosphere. Burial of organic matter and hydrogen escape to space release oxygen. This creates a positive feedback loop because a higher oxidation state leads to more efficient respiration and more photosynthesis, which leads to more burial and escape. The zero contour in Fig. 2 represents a series of equilibrium states with increasing oxidation of Earth's surface amplified by the change from anaerobic to aerobic respiration. The model was forced to be consistent with observation in four respects: First, the oxidation of the surface begins to rise when bacteria first appear, 3700 Ma before the present. Second, The GOE appears 2300 Ma before the present. Third, the duration of the transition is in the ~30 Ma range. And fourth, the tipping point has the O_2 partial pressure in the 1-3 mbar range, which spans the Pasteur point, where microorganisms adapt from fermentation to aerobic respiration.

Understanding the 1.4 Ga delay from the first bacteria to the rise of O_2 is as much a challenge as the suddenness of the rise. The length of the delay suggests primarily a geological process – slow filling of some large geologic reservoir until a tipping point is reached. An example is increasing the partial pressure of O_2 to the Pasteur point, i.e., from 0 to 1.2 mbar, which requires adding 6.2×10^{15} kg of oxygen to the atmosphere. But at current rates, the reduced volcanic gases (Carn et al., 2017) could absorb O_2 at a rate of ~125 TgO/yr, and could absorb 1.2 mbar in $5 \pm 3 \times 10^4$ yr. On a per atom basis, this assumes 4 O for H_2S, 1 O for SO_2, and 4 O for CH_4 , with H_2O, CO_2, and SO_4^{2-} as end products. CH_4 accounts for 90% of the emissions and almost all of the uncertainty (Thornton et al., 2021). The contribution of fumaroles and seeps is not included in these estimates, but it is potentially large (Petrenko et al., 2017).

Thus, using modern volcanic emissions for the filling rates, supplying the 1.2 mbar atmosphere fails by 4.5 orders of magnitude to account for the delay. Sulfate in the ocean is a much larger oxygen reservoir and does 300 times better than the atmosphere. Again using 4 O to oxidize H_2S to SO_4^{2-}, and using 29 mM/l as the concentration of SO_4^{2-} in the ocean, one finds about 2 x 10^{18} kg of oxygen in sulfate. However, the reduced volcanic gases could absorb this oxygen in 0.016 Ga. Banded iron is an even smaller reservoir. In 2022 the proven reserves of iron were 1.8 x 10^{14} kg (Tuck, 2023). Iron ore is roughly equal parts Fe_2O_3 and Fe_3O_4. Creating this ore from FeO requires either $^{1}/_{2}O$ or $^{1}/_{3}O$ per atom of Fe, respectively. This requires only 4 x 10^{13} kg of oxygen, which could be absorbed by the reduced volcanic gases in 320 years, a human not a geologic time scale.

However, current rates may overestimate the reduced volcanic gas emissions in the Archean and therefore may underestimate the delay from the first bacteria to the rise of O_2. This is because the reduced volcanic gas emissions may be mostly recycled organic matter. It is likely that less organic matter, perhaps orders of magnitude less, was being made before the GOE, when the atmosphere was anoxic, than in today's oxygen-saturated atmosphere. Consistent with the recycling idea, an evaluation of modern carbon fluxes in subduction zones suggests that most of the carbon is transported into the mantle lithosphere and crust and not into the convecting mantle, which is much deeper (Kelemen and Manning, 2015). Therefore the mantle + ocean + atmosphere is an important reservoir for carbon and by inference, oxygen, that has increased over Earth history.

The crust and upper mantle are a much larger reservoir than the oceans and atmosphere, but there are unanswered questions: What might cause the oxygen fugacity of these regions to increase during the 1.4 Ga between the appearance of cyanobacteria and the GOE? What is the chemical nature of the change? How does the change affect the surface reservoirs? The top-down answer is oxygenation originating in the atmosphere, either by hydrogen escape or oxygenic photosynthesis. The bottom-up answer is burial of organic matter accompanied by separation of reduced carbon from oxidized carbon within the mantle, and transport of the latter to the upper mantle and crust.

Neither of the top-down mechanisms has an explicit tipping point, and not all details have been worked out. The rate of hydrogen escape is proportional to the abundance of CH_4 in the atmosphere (Catling et al., 2001). But in the low-O_2 Archean atmosphere, with CH_4 the dominant trace constituent, the O_2 would have been rapidly consumed. If the result is H_2O and CO_2 , the process will have little effect on the fugacity of the atmosphere. The other top-down mechanism, oxygenic photosynthesis before the GOE, with burial of organic matter to oxidize the surface, runs counter to evidence of anoxic conditions before the GOE.

The bottom-up mechanism involves subduction, which is responsible for 5.25 km^3/yr of crustal loss (Stern, 2011). Over 1.4 Ga, this is equivalent to a layer covering Earth's surface to a depth of 14.4 km. For comparison, the boundary between the crust and mantle is at ~7 km depth under the oceans and ~30 km depth under the continents. Subduction zone earthquakes occur at depths up to 600 km (Kirby et al., 1996), indicating that down-going slabs sometimes go that deep. With 3000 kg/m^3 as the density, a small fraction, 0.9 x 10^{-4}, of organic matter in the subducting slab would be sufficient to balance the emission rate of reduced volcanic gases. Specifically, the reduced carbon resulting from the transport of organic matter to depths greater than 250 km is mostly graphite and diamond (Duncan and Dasgupta, 2017; Hayes and Waldbauer, 2006), and the oxidized carbon rising to the surface is predominately CO_2. Organic matter, represented by CH_2O, can decompose into $\frac{1}{2}CO_2$ and $\frac{1}{2}CH_4$. The CH_4 component in reduced volcanic gases is partly from decomposition of organic matter and partly primordial, i.e., left over from planetary formation. Modern volcanic gases have about equal parts CO_2 and CH_4. The problem is, if the crust and upper mantle have been steadily oxidizing for the past 3.8 Ga, a massive electron acceptor like sulfate or ferric iron has not been identified (Hayes and Waldbauer, 2006). As discussed earlier, the obvious iron ore at the surface of the Earth is inadequate to absorb the reduced volcanic gases over 1.4 Ga.

There have been successes and failures in using geochemical data to understand the ancient Earth. Dating the appearance of O_2 from the isotopes of sulfur is a big success (Farquhar et al., 2000). Discovering frequent shifts in the ratio of organic carbon to inorganic carbon using the $^{13}C/^{12}C$ ratio is another success (Hayes and Waldbauer, 2006), although causes and effects are unknown. Estimating the time to equilibrate oxidation of shallow crust to fluctuations in atmospheric fugacity using Mn isotopes is a also a success (Hummer et al., 2022). Yet geochemical and biological evidence for whiffs of atmospheric O_2 before the GOE are highly controversial (Olson, 2006): Different data sets give different conclusions. The strongest evidence for life in the Archean comes not from geochemistry but from stromatolites (Bosak et al., 2013).

This work is based on a number of assumptions – that cyanobacteria existed 1.4 Ga before the GOE, and it lasted only 20-50 Ma; that the precipitous change was not due to external forcing like colliding continents, extensive volcanism, climate change, or asteroid impact; that the 1.4 Ga delay was not due to slow evolution of the genetic code, because strictly biological time scales are much too short. This led to the idea of feedbacks and tipping points – that the delay was the time spent oxidizing the crust, upper mantle, ocean and atmosphere; that the tipping point was when the partial pressure of O_2 in the atmosphere crossed the Pasteur point, which is around 1.2 mbar, and the cyanobacteria switched from anaerobic to aerobic metabolism; and that the GOE was result of feedback between atmospheric O_2 and the efficiency of photosynthesis.

Acknowledgement

This research was supported by NASA under grant/cooperative agreement number 80NSSC20K0555 and by Caltech under Provost Academic Programs.

References

Battistuzzi, F.U., Feijao, A., Hedges, S.B., 2004. A genomic timescale of prokaryote evolution: insights into the origin of methanogenesis, phototrophy, and the colonization of land. BMC Evol. Biol. 4, 44. https://doi.org/10.1186/1471-2148-4-44

Bosak, T., Knoll, A.H., Petroff, A.P., 2013. The meaning of stromatolites, in: Jeanloz, R. (Ed.), Annual Review of Earth and Planetary Sciences, Vol. 41. Annual Reviews, Palo Alto, pp. 21–44. https://doi.org/10.1146/annurev-earth-042711-105327

Budyko, M., 1969. Effect of solar radiation variations on climate of Earth. Tellus 21, 611-. https://doi.org/10.3402/tellusa.v21i5.10109

Cadle, R., 1980. A comparison of volcanic with other fluxes of atmospheric trace gas constituents. Rev. Geophys. 18, 746–752. https://doi.org/10.1029/RG018i004p00746

Carn, S.A., Fioletov, V.E., McLinden, C.A., Li, C., Krotkov, N.A., 2017. A decade of global volcanic SO2 emissions measured from space. Sci Rep 7, 44095. https://doi.org/10.1038/srep44095

Catling, D.C., Zahnle, K.J., McKay, C.P., 2001. Biogenic methane, hydrogen escape, and the irreversible oxidation of early Earth. Science 293, 839–843. https://doi.org/10.1126/science.1061976

Duncan, M.S., Dasgupta, R., 2017. Rise of Earth’s atmospheric oxygen controlled by efficient subduction of organic carbon. Nat. Geosci. 10, 387-+. https://doi.org/10.1038/NGEO2939

Falkowski, P.G., Godfrey, L.V., 2008. Electrons, life and the evolution of Earth’s oxygen cycle. Philos. Trans. R. Soc. B-Biol. Sci. 363, 2705–2716. https://doi.org/10.1098/rstb.2008.0054

Farquhar, J., Bao, H.M., Thiemens, M., 2000. Atmospheric influence of Earth’s earliest sulfur cycle. Science 289, 756–758. https://doi.org/10.1126/science.289.5480.756

Farquhar, J., Zerkle, A.L., Bekker, A., 2011. Geological constraints on the origin of oxygenic photosynthesis. Photosynth. Res. 107, 11–36. https://doi.org/10.1007/s11120-010-9594-0

Field, C.B., Behrenfeld, M.J., Randerson, J.T., Falkowski, P., 1998. Primary production of the biosphere: Integrating terrestrial and oceanic components. Science 281, 237–240. https://doi.org/10.1126/science.281.5374.237

Flurkey, W.H., 2010. Yield of ATP molecules per glucose molecule. J. Chem. Educ. 87, 271–271. https://doi.org/10.1021/ed800102g

Goldblatt, C., Lenton, T.M., Watson, A.J., 2006. Bistability of atmospheric oxygen and the Great Oxidation. Nature 443, 683–686. https://doi.org/10.1038/nature05169

Havaux, M., 2020. Plastoquinone in and beyond photosynthesis. Trends Plant Sci. 25, 1252–1265. https://doi.org/10.1016/j.tplants.2020.06.011

Hayes, J.M., Waldbauer, J.R., 2006. The carbon cycle and associated redox processes through time. Philos. Trans. R. Soc. B-Biol. Sci. 361, 931–950. https://doi.org/10.1098/rstb.2006.1840

Hummer, D.R., Golden, J.J., Hystad, G., Downs, R.T., Eleish, A., Liu, C., Ralph, J., Morrison, S.M., Meyer, M.B., Hazen, R.M., 2022. Evidence for the oxidation of Earth’s crust from the evolution of manganese minerals. Nat. Commun. 13, 960. https://doi.org/10.1038/s41467-022-28589-x

Ingersoll, A., 1969. Runaway greenhouse - A history of water on Venus. J. Atmos. Sci. 26, 1191-+. https://doi.org/10.1175/1520-0469(1969)026<1191:TRGAHO>2.0.CO;2

Kelemen, P.B., Manning, C.E., 2015. Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. Proc. Natl. Acad. Sci. U. S. A. 112, E3997–E4006. https://doi.org/10.1073/pnas.1507889112

Kirby, S.H., Stein, S., Okal, E.A., Rubie, D.C., 1996. Metastable mantle phase transformations and deep earthquakes in subducting oceanic lithosphere. Rev. Geophys. 34, 261–306. https://doi.org/10.1029/96RG01050

Kirchhoff, H., 2014. Diffusion of molecules and macromolecules in thylakoid membranes. Biochimica et Biophysica Acta (BBA) - Bioenergetics, Dynamic and ultrastructure of bioenergetic membranes and their components 1837, 495–502. https://doi.org/10.1016/j.bbabio.2013.11.003

Kuhl, M., Glud, R.N., Ploug, H., Ramsing, N.B., 1996. Microenvironmental control of photosynthesis and photosynthesis-coupled respiration in an epilithic cyanobacterial biofilm. J. Phycol. 32, 799–812. https://doi.org/10.1111/j.0022-3646.1996.00799.x

Luo, G., Ono, S., Beukes, N.J., Wang, D.T., Xie, S., Summons, R.E., 2016. Rapid oxygenation of Earth's atmosphere 2.33 billion years ago. Sci. Adv. 2, e1600134. https://doi.org/10.1126/sciadv.1600134

Olson, J.M., 2006. Photosynthesis in the Archean Era. Photosynth. Res. 88, 109–117. https://doi.org/10.1007/s11120-006-9040-5

Paumann, M., Regelsberger, G., Obinger, C., Peschek, G.A., 2005. The bioenergetic role of dioxygen and the terminal oxidase(s) in cyanobacteria. Biochim. Biophys. Acta-Bioenerg. 1707, 231–253. https://doi.org/10.1016/j.bbabio.2004.12.007

Petrenko, V.V., Smith, A.M., Schaefer, H., Riedel, K., Brook, E., Baggenstos, D., Harth, C., Hua, Q., Buizert, C., Schilt, A., Fain, X., Mitchell, L., Bauska, T., Orsi, A., Weiss, R.F., Severinghaus, J.P., 2017. Minimal geological methane emissions during the Younger Dryas–Preboreal abrupt warming event. Nature 548, 443–446. https://doi.org/10.1038/nature23316

Ploug, H., 2008. Cyanobacterial surface blooms formed by Aphanizomenon sp and Nodularia spumigena in the Baltic Sea: Small-scale fluxes, pH, and oxygen microenvironments. Limnol. Oceanogr. 53, 914–921. https://doi.org/10.4319/lo.2008.53.3.0914

Schopf, J.W., 2014. Geological evidence of oxygenic photosynthesis and the biotic response to the 2400-2200 Ma "Great Oxidation Event." Biochem.-Moscow 79, 165–177. https://doi.org/10.1134/S0006297914030018

Shimakawa, G., Kohara, A., Miyake, C., 2021. Characterization of light-enhanced respiration in cyanobacteria. Int. J. Mol. Sci. 22, 342. https://doi.org/10.3390/ijms22010342

Slotznick, S.P., Johnson, J.E., Rasmussen, B., Raub, T.D., Webb, S.M., Zi, J.-W., Kirschvink, J.L., Fischer, W.W., 2022. Reexamination of 2.5-Ga "whiff" of oxygen interval points to anoxic ocean before GOE. Sci. Adv. 8, eabj7190. https://doi.org/10.1126/sciadv.abj7190

Soo, R.M., Hemp, J., Parks, D.H., Fischer, W.W., Hugenholtz, P., 2017. On the origins of oxygenic photosynthesis and aerobic respiration in Cyanobacteria. Science 355, 1436–1439. https://doi.org/10.1126/science.aal3794

Staal, M., Hekkert, S.T.L., Harren, F.J.M., Stal, L.J., 2003. Effects of O-2 on N-2 fixation in heterocystous cyanobacteria from the Baltic Sea. Aquat. Microb. Ecol. 33, 261–270. https://doi.org/10.3354/ame033261

Stal, L.J., Moezelaar, R., 1997. Fermentation in cyanobacteria. Fems Microbiol. Rev. 21, 179–211. https://doi.org/10.1016/S0168-6445(97)00056-9

Stern, C.R., 2011. Subduction erosion: Rates, mechanisms, and its role in arc magmatism and the evolution of the continental crust and mantle. Gondwana Res. 20, 284–308. https://doi.org/10.1016/j.gr.2011.03.006

Thornton, B.F., Etiope, G., Schwietzke, S., Milkov, A., Klusman, R.W., Judd, A., Oehler, D.Z., 2021. Conflicting estimates of natural geologic methane emissions COMMENT. Elementa-Sci. Anthrop. 9, 00031. https://doi.org/10.1525/elementa.2021.00031

Tuck, C.C., 2023. Iron Ore, in: Mineral Commodity Summaries 2023. U. S. Geological Survey, pp. 98–99.

Waldbauer, J.R., Newman, D.K., Summons, R.E., 2011. Microaerobic steroid biosynthesis and the molecular fossil record of Archean life. Proc. Natl. Acad. Sci. U. S. A. 108, 13409–13414. https://doi.org/10.1073/pnas.1104160108

Ward, L.M., Kirschvink, J.L., Fischer, W.W., 2016. Timescales of Oxygenation Following the Evolution of Oxygenic Photosynthesis. Orig. Life Evol. Biosph. 46, 51–65. https://doi.org/10.1007/s11084-015-9460-3

Precambrian Research

Supplementary Material
for

The Great Oxidation Event (GOE): Biogeochemical Feedback and Tipping Points

Andrew P. Ingersoll
Division of Geological and Planetary Sciences
California Institute of Technology
Pasadena, CA 91125
api@caltech.edu

Contents

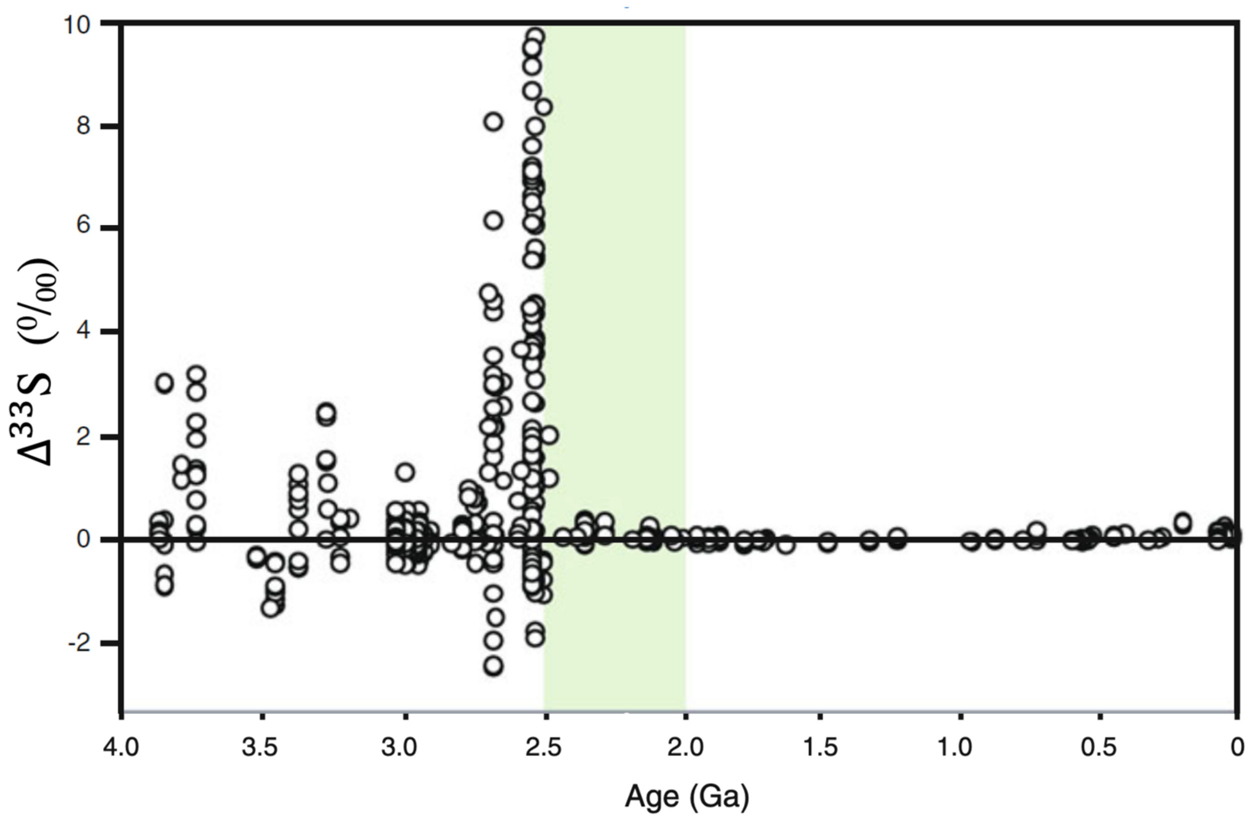

Figure 5 of Farquhar et al. (2011). The points are samples of sulfur from sediments at different places around the world. Radioactive elements in the sediment provide the age. Three isotopes of sulfur are used to determine the amount $\Delta^{33}S$ of mass-independent fractionation. The graph shows a sudden shift to mass-dependent fractionation ~2.3 Ga before the present. The dominant fractionation processes are thought to involve chemistry of volcanic gases H_2S and SO_2 before the event and chemistry of sulfate SO_4^{2-} after, signifying the sudden appearance of molecular oxygen.

Farquhar, J., Zerkle, A. L., & Bekker, A. (2011). Geological constraints on the origin of oxygenic photosynthesis. *Photosynthesis Research*, *107*(1), 11–36. https://doi.org/10.1007/s11120-010-9594-0

Caltech Ge 103 Climate Feedback Homework Andrew Ingersoll

Feedback occurs when the output affects the input and/or the processor. In climate models, output is the temperature. Absorbed sunlight and infrared emission are the input. Negative feedback tends to damp the response to a change in input. Infrared emission is an example: The hotter it gets, the faster the planet loses heat, since the latter goes as σT^4, and that causes the planet to cool down. Positive feedback tends to amplify the response. The first example is ice-albedo feedback: The colder it gets, the more ice and snow accumulate; the albedo goes up, and more sunlight is reflected to space, causing the planet to get even colder. It amplifies the heating if you make the planet warmer at the start, too. The second example is water vapor feedback: The warmer it gets, the more water vapor goes into the atmosphere, which means the infrared optical depth of the atmosphere is greater, trapping the heat and causing the planet to get even warmer. The first is associated with snowball Earth and possibly the polar ice caps of Mars, and the second is associated with the runaway greenhouse on Venus. These two positive feedbacks operate on the present-day Earth to make the climate more sensitive to changes in the forcing.

1. Consider the globally averaged energy balance equation for a planet whose surface temperature is T. The solar flux is F_0, but it is spread over the surface area of the sphere, which is 4 times the cross-sectional area, so the equation is

$$C\frac{dT}{dt} = \frac{F_0}{4}\left[1 - A(T)\right] - \varepsilon(T)\sigma T^4, \quad \varepsilon = \frac{1}{\left[1+\tau^*(T)\right]} \tag{1}$$

The feedback is contained in the albedo A(T) and the infrared optical depth $\tau^*(T)$. Here ε is the emissivity – the emission to space divided by the blackbody emission of the surface. When you add greenhouse gases to the atmosphere, $\tau^*(T)$ increases and less of the surface heat flux gets out – less is radiated to space. The heat capacity of the system (energy/area/K) is *C*. Its value depends on whether the heat storage involves the deep ocean, the upper ocean, or just the atmosphere. The solar flux is not necessarily constant, and we will be interested in how T varies as a function of F_0 and time.

2. Turn off both feedbacks and let A = 0.29 and τ^* = 0.63, both constant. The emissivity is therefore 1/1.63. These values match the current equilibrium for Earth, for which dT/dt = 0, F_0 = 1367 W m^{-2} , $\sigma = 5.67 \times 10^{-8}$ W m^{-2} K^{-4}, and T ≈ 289 K. Define $T_0 = [F_0/(4\sigma)]^{1/4}$, which is a measure of the solar forcing—the input. Then T is a measure of the response—the output. Equation (1) can be written

$$\frac{dT}{dt} = \frac{\sigma}{C}\left[T_0^4(1-A) - \varepsilon T^4\right] \tag{2}$$

Using your favorite math package (Mathematica, Maple, Matlab, IDL/ENVI), you should generate a contour plot of the right-hand side. The abscissa is T_0 and the ordinate is *T*. Initially the graph should cover the range 220 K to 320 K in both directions. The contours are proportional to *dT/dt*. Label the contours in degrees per day, using $C = \int C_P \rho dz = C_P P / g$, where C_P =1000 J K^{-1} kg^{-1} is the specific heat of air, ρ is the density, $P = 10^5$ Pa is the surface pressure, and g = 10 m s^{-2} is the gravitational acceleration. This value of C applies if the ocean is not involved in heat storage, and it would apply to a planet without an ocean. A planet, not necessarily in equilibrium, at a given temperature and a given distance from the sun defines a point on the graph. The contour value at that point shows how the planet evolves. A positive value means that the planet's temperature rises—it moves upward on the graph. A negative value means that the temperature falls—it moves downward on the graph. The positive and negative values are separated by the equilibrium solution, where *dT/dt* = 0. Locate the present Earth (T ≈ 289 K), assuming it is in equilibrium, and find the corresponding value of T_0. Verify that it is the value you expect, i.e., it corresponds to the current value of the solar constant. Find the contours for which *dT/dt* = ±1 degree per day. Is the present Earth solution stable or unstable?

Note: A steady solution has *dT/dt* = 0. It is an equilibrium solution because the terms balance. The equilibrium may be either stable or unstable. It is stable if the system returns back toward the steady solution or oscillates about the steady solution when you perturb it. The solution is unstable if the system moves away from the steady solution when you perturb it. Think of a rigid pendulum at the bottom of its swing and a rigid pendulum at the top of its swing. They both are steady solutions, but only one of them is stable.

3. Now add ice-albedo feedback by introducing the function A(T), which is chosen to match data on albedo and temperature as functions of latitude on the current Earth. Think about why this is a dangerous assumption, but then proceed. An expression that matches the data is

$$A(T) = 0.47 - 0.25 \tanh\left[(T - 268)/23\right] \tag{3}$$

This gives A = 0.29 when T ≈ 289 and approaches A = 0.22 at high T and A = 0.72 at low T. Equation (2) still applies, but now A = A(T) according to Eq. (3). The emissivity ε is still a constant equal to 1/1.63. As before, locate the present Earth (T ≈ 289 K), assuming it is in equilibrium, and find the corresponding value of T_0. You may have to zoom in on this point to get an accurate estimate of T_0. Verify that it is the value you expect, i.e., it corresponds to the current value of the solar constant. Notice that there are two other equilibrium solutions for the same T_0. One is the snowball Earth solution and the other is an unstable solution.

4. You should verify that the middle part of the equilibrium curve is unstable by examining the sign of *dT/dt* on either side of the curve. In the same way, you should verify that the top and bottom parts are stable. In other words, show that the sign of *dT/dt* is such that the system moves away from the unstable solution and moves toward the snowball Earth solution and toward the present-day (warm Earth) solution. Notice, however, that the warm Earth solution disappears if we reduce the solar constant by a little bit. Then the snowball Earth solution is the only equilibrium solution. Estimate the value of T_0 for which the warm-Earth solution ceases to exist, called a "tipping point" in the global warming debate. Once the Earth is in the snowball Earth state, it is hard to get back. What is the value of T_0 for which the snowball Earth solution ceases to exist? This is an example of hysteresis – behavior where the current equilibrium state of a system depends on its recent history.

M. I. Budyko (1956 in Russian, 1992 in English) developed ice-albedo feedback models that predicted an ice-covered Earth when the radiative heating dropped below a certain value. Joe Kirschvink (1990) presented geologic evidence that such an event actually happened, and he coined the term “snowball Earth.” The question then is, how did the Earth ever get out of the snowball state? Geologists argue that reduced weathering of igneous rocks during snowball conditions leads to less release of Ca^{++} to the oceans and therefore less precipitation of $CaCO_3$. This allows the CO_2 from volcanoes to accumulate and warm the atmosphere. Conversely, increased weathering during warm conditions increases the precipitation of $CaCO_3$ and decreases the amount of atmospheric CO_2. This reduces the greenhouse effect and allows the Earth to cool. The carbonate cycle is a negative feedback, and it stabilizes the climate. It’s a nice idea, but it doesn’t explain why the climate should oscillate from one state to another.

5. Now turn off the ice-albedo feedback and let A = 0.29. Obviously I am “tuning” the numbers to make them match current conditions, and I haven’t figured out how to combine the two feedbacks. When I do, the present Earth is always in an unstable equilibrium. Let $\tau^*(T)$ include a variable part that is proportional to the vapor pressure of water and a constant part due to everything else (other greenhouse gases and clouds):

$$\tau^*(T) = 0.56 + 0.07\exp\left[5413\left(\frac{1}{288} - \frac{1}{T}\right)\right] \qquad (4)$$

The number 5413 is L/R, where L is the latent heat of vaporization of water (2.5 x 10^6 J/kg), and R is the universal gas constant (8.314 J mol^{-1} K^{-1}) divided by the molecular mass of water (0.018 kg mol^{-1}). The exponential is a reasonably good approximation to e(T)/e(288 K), where e(T) is the saturation vapor pressure (SVP) of water. This assumes there is an ocean that maintains the saturation of the atmosphere, so it doesn't apply to present-day Venus. With this assumption, Eq. (2) can be written

$$\frac{dT}{dt} = \frac{\sigma}{C}\left[T_0^4(1-0.29) - \frac{T^4}{\left(1+\tau^*(T)\right)}\right] \qquad (5)$$

Again you should create a contour plot of the right hand side. Good limits for T are $260 < T < 360$ K. Find the equilibrium curve, for which $dT/dt = 0$, and find the present day Earth on this curve. Show that the present-day Earth is stable. Find the unstable solution that exists for the same value of the solar constant – the same value of T_0 as today. This solution is hotter than the present warm-Earth solution. At what value of T_0 does the warm-Earth solution cease to exist? Show that there is no stable equilibrium for an Earth-like planet at the orbit of Venus.

Venus is unstable in this model because we assumed an infinite reservoir of water at the surface. In reality, once the oceans boil away and you have a 261-bar atmosphere (~ 260 parts water vapor to 1 part dry air), the feedback stops because τ^* can’t increase any more. The infrared optical depth will be huge, and the surface temperature will be huge as well (some estimates say 1500 K), but the system will be in equilibrium. This is the final state of the runaway greenhouse. I coined the term in a paper (Ingersoll, 1969) that was an outgrowth of a homework assignment in the first course I ever taught at Caltech. The homework didn't work because the present-Earth solution was unstable for the parameters I used. Equation (4) is a toned-down version that does work. In the paper I argued that the radiation shield of nitrogen and oxygen that prevents UV radiation from reaching water vapor on the present Earth would not operate if water vapor were the major atmospheric constituent (i.e., more than 50%; today its abundance is 2 x 10^{-6} in the stratosphere). Instead, water would be photodissociated, the hydrogen would escape to space, and the oxygen would combine with surface rocks.

Escape of hydrogen was my explanation for why Venus has virtually no water today. Evidence in favor of this model is that the D/H ratio on Venus is 150 times greater than on Earth. Fractionation of hydrogen isotopes occurs because escape to space is mass-dependent, and when a large amount of hydrogen escapes, the heavier deuterium is preferentially left behind. The fractionation factor is uncertain by orders of magnitude, however, so the amount of water lost is equally uncertain.

Later I tried to create a homework assignment that started with an ocean of water and evolved to the present D/H value for Venus. The problem was that D is twice as massive as H, which has a huge effect when you put it inside a negative exponential ─ the high-energy tail of the Maxwell-Boltzmann distribution, so the model kept giving unrealistically high values of D/H. I could solve the problem by continuously adding water with an Earth-like ratio of D/H. Then I discovered that David Grinspoon (1993) had already done that. Such water might come from the mantle of Venus or from comets. Other elements and their isotopes may help us identify the source.

Budyko, M., Yefimova, N., Aubenok, L., & Strokina, L. (1962). The Heat-Balance of the Surface of the Earth. *Soviet Geography Review and Translation*, *3*(5), 3–16. https://doi.org/10.1080/00385417.1962.10769936

Grinspoon, D. (1993). Implications of the high D/H Ratio for the sources of water in Venus atmosphere. *Nature*, *363*(6428), 428–431. https://doi.org/10.1038/363428a0

Ingersoll, A. (1969). Runaway greenhouse - A history of water on Venus. *Journal of the Atmospheric Sciences*, *26*(6), 1191–1198. https://doi.org/10.1175/1520-0469(1969)026<1191:TRGAHO>2.0.CO;2

Kirschvink, J. L., Gaidos, E. J., Bertani, L. E., Beukes, N. J., Gutzmer, J., Maepa, L. N., & Steinberger, R. E. (2000). Paleoproterozoic snowball Earth: Extreme climatic and geochemical global change and its biological consequences. *Proceedings of the National Academy of Sciences of the United States of America*, *97*(4), 1400–1405. https://doi.org/10.1073/pnas.97.4.1400