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What caused the rise of atmospheric O_2?

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ABSTRACT

Oxygenic photosynthesis appears to have evolved well before O_2 levels increased in the atmosphere, at around 2.4 Ga. This has led to numerous suggestions as to what may have kept O_2 suppressed and then eventually allowed it to rise. These suggestions include changes in the recycling of carbon and sulfur relative to water (or hydrogen), a switch from dominantly submarine to dominantly subaerial volcanism, gradual oxidation of the continents and a concomitant decrease in reduced metamorphic gases, a decline in deposition of banded iron-formations, a decline in nickel availability, and various proposals to increase the efficiency of photosynthesis. Several of these different mechanisms could have contributed to the rise of O_2, although not all of them are equally effective. To be considered successful, any proposed mechanism must make predictions that are consistent with the carbon isotope record in marine carbonates, which shows relatively little change with time, apart from transient (but occasionally spectacular) excursions. The reasons for this constancy are explored here, but are not fully resolved. In the process of making these comparisons, a self-consistent redox balance framework is developed which will hopefully prove useful to others who may work on this problem and to astronomers who may one day try to decipher spectral signatures of oxygen on Earth-like exoplanets.

Contents

1. Introduction

It gives me great pleasure to contribute to a volume honoring Dick Holland. Dick was one of my greatest scientific mentors during my

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career, along with Jim Walker and Jim Pollack. Jim Walker actually suggested to me some thirty years ago that I needed to meet Dick because we all three shared an interest in atmospheric evolution. Dick and I did meet at an AGU carbon cycle meeting in Tarpon Springs, Florida, back in 1984, and we remained in more or less constant scientific communication until shortly before his death. Our conversations, including several during Dick's last year, have been a continuing source of inspiration.

When Dick and I got together, talk invariably revolved around the topic of early atmospheric composition and, in recent years, the cause of the rise of atmospheric O_2. Dick, of course, devoted a large segment of his scientific career to this subject. He was a very good geochemist and had an encyclopedic knowledge of the geochemical literature surrounding this question. In the old days, prior to the revelations from the sulfur MIF record published by Farquhar et al. (2000), much of the debate was about when exactly atmospheric O_2 rose and how low it might have been prior to that time. Since Farquhar's paper, most workers agree that O_2 rose for the first time between 2.33 Ga and 2.45 Ga (Bekker et al., 2004), although transient increases may have occurred just before that time (Anbar et al., 2007). But the question of exactly *why* O_2 levels rose at this time continues to provoke debate. The question is complicated, because most researchers think that cyanobacteria were producing O_2 well before the so-called "Great Oxidation Event", or GOE, at 2.45 Ga. This argument is based on several different lines of geologic evidence, including organic biomarkers in sediments (*e.g.* Brocks et al., 1999; Summons et al., 1999), carbon isotope patterns (Hayes, 1983; Hayes, 1994), trace metal anomalies (Anbar et al., 2007), and stromatolite morphology (Bosak et al., 2009). I will not develop these arguments fully here, as they have been discussed in detail by various authors (*e.g.* Canfield, 2005; Claire et al., 2006; Holland, 2006; Farquhar et al., 2011). In truth, the evidence is not as solid as one might wish, and other authors continue to dispute this claim (Liang et al., 2006; Kirschvink and Kopp, 2008). But if even a few of the remaining arguments are correct, then the question of what caused the rise of atmospheric O_2 has been turned on its head. We now ask: What was it that *delayed* the rise of O_2? These questions are, of course, closely related, because once the reason for the delay went away, then O_2 was free to rise.

Dick himself proposed a detailed hypothesis to address this question (Holland, 2002, 2009). His mechanism involves changes in the amount of carbon and sulfur relative to hydrogen in volcanic gases caused by increased recycling as the Earth matured. I will discuss this hypothesis in some detail because it does indeed appear to be an important part of the answer, although my interpretation of how it works is slightly different than Dick's. Others have offered a variety of different hypotheses to explain the rise of O_2. Hunten and Donahue (1976) pointed out that escape of hydrogen to space should leave behind oxygen that might have oxidized iron in Earth's crust, eventually leading to O_2 accumulation. I myself believed for many years that the upper mantle became progressively more oxidized as a result of loss of hydrogen to space, causing volcanic gases to also become more oxidized with time (Kasting et al., 1993). But this hypothesis was dealt a severe blow by measurements of Cr and V in ancient basalts, which showed that the redox state of the upper mantle has remained approximately constant since 3.5 Ga, or even earlier (Canil, 1997; Delano, 2001; Canil, 2002; Li and Lee, 2004; Trail et al., 2011). So, I will not discuss that hypothesis further here. Since then, the number of different hypothesis for triggering the GOE has proliferated. Catling et al. (2001) and Claire et al. (2006) suggested that hydrogen escape to space caused oxidation of the *continents*, not the mantle, and this resulted in a gradual decrease over time in reduced metamorphic gases. Kump and Barley (2007), and later Gaillard et al. (2011), proposed that the rise of O_2 was caused by a gradual switch from submarine to subaerial outgassing, which caused volcanic gases to become more oxidized with time. Isley and Abbott (1999) suggested that the GOE was linked to a decrease in deposition of banded iron-formations, which may itself have been linked to the end of a period of enhanced mantle plume activity (Barley et al., 2005). Konhauser et al. (2009) suggested that a decrease in Ni availability in the Late Archean led to a decrease in methanogenesis, which in turn led to the rise in O_2. Don Canfield and I have proposed a mechanism that involves changes in the rate of serpentinization of continents and seafloor, along with possible biological innovations, specifically, the evolution of nitrogenase protection mechanisms in cyanobacteria (Kasting and Canfield, 2012) (see also Anbar and Knoll (2002) and Grula (2005)). A related proposal involves productivity increased caused by changes in the availability of Mo and V (Zerkle et al., 2006; Scott et al., 2008, 2011). Each of these hypotheses is discussed in some detail in the sections that follow.

Several of the proposals mentioned above do not explicitly involve biology. That may seem surprising, because the rise of atmospheric O_2 is universally attributed to the invention of oxygenic photosynthesis by *cyanobacteria* (see, *e.g.*, Cloud, 1972; Walker, 1977). Cyanobacteria are single-celled true Bacteria that are widely believed to have been the first oxygenic photosynthesizers on the planet. The evidence for this is indisputable: the chloroplasts of algae and higher plants contain DNA that, when sequenced, puts them together with cyanobacteria on a single branch of the "universal" (ribosomal RNA) tree of life (Margulis, 1982). As already mentioned, though, oxygenic photosynthesis appears to have originated several hundred million years prior to the GOE, so that event cannot by itself be credited with causing the O_2 rise. Furthermore, from a geochemists' standpoint, the global redox budget had to be balanced both before and after the GOE, regardless of when oxygenic photosynthesis was invented. Trying to explain that is what the remainder of this paper is about.

2. The global redox budget

2.1. Defining the budget

Based on the perception that cyanobacteria appeared well before the GOE, various authors have proposed that the rise of O_2 was delayed by some geochemical mechanism: the sinks for O_2 outweighed its sources. To analyze this problem quantitatively, let us start by defining the *global redox budget* as the redox budget of the combined atmosphere–ocean system. Hayes and Waldbauer (2006) carried out a similar exercise for Earth's redox budget, but they included the crust, as well. That would not be appropriate for the problem being considered here, as the time scale for oxidizing the crust is hundreds of millions to billions of years, whereas the lifetime of O_2 in the atmosphere–ocean system today is only ~2 million years (Holland, 1984). The lifetime of H_2 in the Archean atmosphere–ocean system was even shorter, only ~30,000 years. (This is easily demonstrated by dividing the column mass of H_2 in a 1-bar atmosphere by the diffusion-limited escape rate of hydrogen to space, given by Eq. (7) below.) Hence, the redox state of the atmosphere–ocean system should remain in quasi-steady state on geological time scales, whereas the redox state of the crust continues to evolve with time.

Today, the atmosphere and the ocean freely exchange O_2, and so the global redox budget is typically described in terms of O_2 sources and sinks (see, e.g., Holland, 2002). On the early Earth, O_2 was scarce (Kasting, 1993) and the atmosphere and ocean would have freely exchanged reduced gases such as H_2 and CH_4. We are interested in the early Earth here, so I will keep track of the global redox budget in terms of H_2 equivalents. These are related to O_2 equivalents by the reaction:

$$2\,H_2 + O_2 \leftrightarrow 2\,H_2O \qquad (1)$$

Thus, 2 mol of H_2 consume 1 mol of O_2, and vice versa. If you prefer to keep track of redox in terms of O_2, just divide all my numbers by 2.

To facilitate the analysis it is convenient to define reference, or "neutral", oxidation states for compounds containing hydrogen, carbon, nitrogen, iron, and sulfur. I take these to be, respectively, H_2O, CO_2, N_2,