LETTERS

Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago

Lee R. Kump[1] & Mark E. Barley[2]

The hypothesis that the establishment of a permanently oxygenated atmosphere at the Archaean–Proterozoic transition (~2.5 billion years ago) occurred when oxygen-producing cyanobacteria evolved[1] is contradicted by biomarker evidence for their presence in rocks 200 million years older[2]. To sustain vanishingly low oxygen levels despite near-modern rates of oxygen production from ~2.7–2.5 billion years ago thus requires that oxygen sinks must have been much larger than they are now. Here we propose that the rise of atmospheric oxygen occurred because the predominant sink for oxygen in the Archaean era—enhanced submarine volcanism—was abruptly and permanently diminished during the Archaean–Proterozoic transition. Observations[3–5] are consistent with the corollary that subaerial volcanism only became widespread after a major tectonic episode of continental stabilization at the beginning of the Proterozoic. Submarine volcanoes are more reducing than subaerial volcanoes[6], so a shift from predominantly submarine to a mix of subaerial and submarine volcanism more similar to that observed today would have reduced the overall sink for oxygen and led to the rise of atmospheric oxygen.

Abundant evidence supports the argument that the atmosphere before ~2.5 billion years ago (~2.5 Gyr ago) was essentially devoid of oxygen[7] (Fig. 1). The strongest argument comes from the presence of sedimentary sulphides with mass-independent fractionation (MIF) only in rocks older than 2.45 Gyr (ref. 8), a phenomenon that requires both the virtual absence ($<10^{-5}$ times the present atmospheric level) of molecular oxygen[9] and an abundance of reducing gases (such as methane[10]) in the atmosphere. The recent recognition of 2.92- and 2.76-Gyr-old sedimentary sulphides without a strong MIF sulphur isotope signature[11,12] supports an earlier suggestion[13] that atmospheric oxygen levels may have increased temporarily before the permanent rise 2.45 Gyr ago, although a collapse of atmospheric methane without a corresponding rise of atmospheric O_2 cannot be ruled out[10].

The lack of any secular trend in the carbon isotopic composition of the ocean, as preserved in limestones, argues against a substantial increase in organic carbon burial (the long-term source of oxygen) between 2.5 and 2.4 Gyr ago[6] (but see ref. 14 for an opposing view). Thus, most explanations focus on a decrease in consumption rate[6,15–17]. The absence of oxidized soil profiles and red beds indicates that oxidative weathering rates were negligible during the Archaean. The likely sinks for oxygen were its reaction with reduced volcanic and metamorphic gases[15] and its reaction with Fe^{2+}, either during hydrothermal alteration of seafloor basalts, or as hydrothermal Fe^{2+} dissolved in anoxic sea water[18].

For volcanic sinks to have been larger in the Archaean than in the post-Archaean, volcanic/metamorphic gases must have been more reducing: even though rates of volcanism were higher in the Archaean, the surficial redox balance would only be tipped towards reducing if these gases were more reduced because, as the carbon isotopes show, the flux of oxygen through organic matter burial scaled up proportionately[6].

The coincidence of the rise of atmospheric O_2 with the Archaean–Proterozoic transition suggests that the stabilization of continental cratons may have affected the volcanic sink for oxygen. Although there is evidence for the existence of 'continental' crust since the Eoarchaean (since 3.6 Gyr ago)[5], the oxygen isotope ratios of igneous zircons[19] and trace-element and isotopic compositions of sedimentary rocks[3] are not consistent with the presence of large, elevated, mature, continental landmasses before 3.0 Gyr ago. The majority of Archaean cratons achieved long-term tectonic stability as elevated continental land masses between 2.7 and 2.5 Gyr ago with buoyant, depleted upper-mantle keels[20] and thermo-mechanically stable

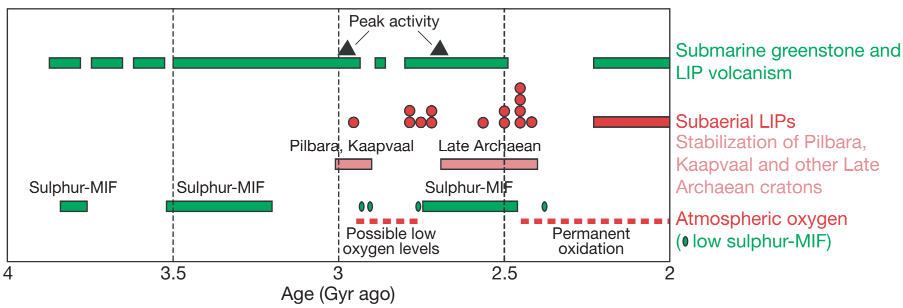

Figure 1 | Archaean–Palaeoproterozoic volcanism, continental stabilization, and atmospheric oxygen evolution. The bars labelled 'Sulphur-MIF' represent evidence of strong MIF of sulphur isotopes. This strong constraint on atmospheric oxygen levels is recorded in three sedimentary sequences 3.85–3.77, 3.5–3.2 and 2.74–2.45 Gyr ago[8]. We note the abrupt and permanent end of the strong MIF signal after 2.45 Gyr ago. The oval symbols indicate well-dated sedimentary sequences with low sulphur-MIF values[8,11,12], consistent with low and rising levels of atmospheric oxygen. This figure is based on Supplementary Tables 1 and 2.

[1]NASA Astrobiology Institute and Department of Geosciences, Pennsylvania State University, 535 Deike Building, University Park, Pennsylvania 16802, USA. [2]School of Earth and Geographical Sciences, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia.

crustal profiles[21]. This occurred during and after a period of mantle plume activity (2.72–2.66 Gyr ago) that resulted in the most prodigious episode of generation and preservation of continental crust in Earth history (Fig. 1). The Pilbara and Kaapvaal cratons achieved tectonic stability during an earlier period of mantle plume activity between 3.0 and 2.9 Gyr ago. Archaean cratons amalgamated to form the first supercontinent or a number of supercratons by the end of the Archaean[13,22,23].

Archaean volcanism seems to have been dominated by submarine eruptions, with greenstone belts characterized by submarine basalt–komatiite successions and dominantly submarine island-arc-like volcanic complexes[24]. Many of the preserved basalt–komatiite successions are mantle-plume-derived large igneous provinces (LIPs; preserved as flood basalts and large mafic dyke swarms). The arc-like successions contain only minor reworked pyroclastic deposits derived from subaerial eruptions, and subaerial andesite volcanoes on thickened continental crust seem to be almost absent in the Archaean. Various explanations for the abundance of Archaean submarine volcanic rocks have been proposed, but most depend on the idea that the Archaean oceanic lithosphere would have been thicker and that isostatic adjustment displaced the oceans onto the continents[25].

In contrast, the preserved Palaeoproterozoic volcanic record is dominated by subaerial continental LIPs[24]. Most Proterozoic greenstone successions resemble Phanerozoic island arc assemblages with a higher proportion of rocks derived from subaerial eruptions than their Archaean counterparts[24].

It is possible that the predominance of immature submarine crust in preserved Archaean cratons is an artefact of selective preservation: only a small fraction of the crust that existed in the Archaean is preserved today. However, if plate tectonics and tectonic recycling operated in a steady-state mode with a near-modern balance of large stable continents and oceans in the Archaean, then one might expect that cratons would be preferentially preserved and immature subduction/accretion terrains would be preferentially destroyed[3], rather than the reverse. Immature tectonic environments were probably the norm in the Archaean, with fragments of evolving proto-continental crust within largely submarine volcanic arcs at convergent plate margins. Because such proto-continental fragments would take several hundred million years to achieve thermo-mechanical stability[5,21], they would have been tectonically weak and recycled at a similar rate to volcanic arcs and oceanic plateaus.

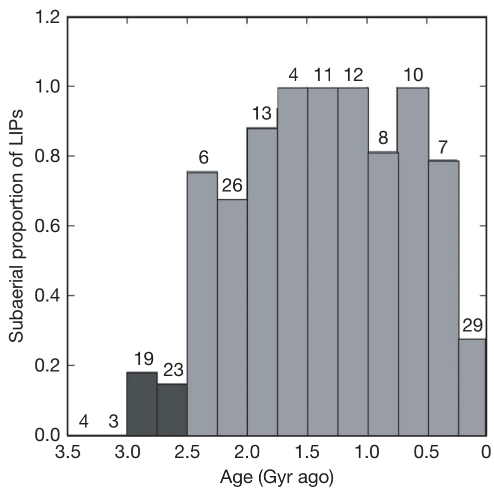

Figure 2 | Secular variation in proportion of subaerial LIPs. Proportion determined as the percentage of the total subaerial LIP occurrences in the age range divided by the sum of the percentage of the total occurrences of both subaerial and submarine LIPs in that age range (see Supplementary Tables 1 and 2). The numbers indicate the total number of LIPs reported. Dark bars reflect Archaean occurrences (before the rise of atmospheric oxygen); light bars reflect post-Archaean occurrences after the rise of atmospheric oxygen. The low proportion over the last 250 million years is probably a preservational bias; no sea floor older than 180 Myr has been preserved.

In summary, although it is possible that the predominance of juvenile crust in the Archaean is a preservational artefact[26], there is considerable evidence to support the opposing view that the transition from an Archaean to modern-day plate-tectonic regime occurred in two major steps, in the Mesoarchaean and at the Archaean–Proterozoic boundary, and that this transformation promoted subaerial volcanism.

A database of LIPs through time[27] and 24 greenstone successions older than 2.0 Gyr provides a further indication of the shift in the balance between submarine and subaerial volcanism (Figs 1 and 2; Supplementary Tables 1 and 2). Archaean greenstone successions contain both submarine continental and oceanic LIPs as well as numerous submarine arc-like volcanic successions. Most pre-2.5-Gyr-ago (Archaean) LIPs and arc-like successions were emplaced during periods of increased mantle plume activity at ~2.95 and ~2.7 Gyr ago, with seven subaerial Archaean flood basalt sequences, ranging in age from 2.94 to 2.71 Gyr old, restricted to the Pilbara and Kaapvaal cratons (which functioned as stable cratons by ~2.9 Gyr ago). In contrast, of the 28 Palaeoproterozoic 2.5–2.0-Gyr-old LIPs listed[27], 25 (89%) are subaerial. Seven dominantly subaerial continental LIPs were emplaced on four cratons between 2.51 and 2.41 Gyr ago, during a period of increased mantle plume activity[4,13]. A subsequent period of increased magmatic activity between 2.24 and 2.0 Gyr ago is recorded by two submarine LIPs, four submarine greenstone successions and 20 subaerial continental LIPs worldwide.

We interpret these data to be consistent with our proposal that the stabilization of Archaean cratons (to form the first large tectonically stable high-standing continents) resulted in a change from dominantly submarine volcanism to a mixture of submarine and subaerial volcanism in tectonic settings and proportions similar to the Phanerozoic Earth. Interestingly, stabilization of the Pilbara and Kaapvaal cratons corresponds to the early occurrence of low-MIF sedimentary sulphides; the Mozaan group in the Kaapvaal craton[12] overlies the 2.94-Gyr-old Pongola subaerial LIP and is similar in age to the Mosquito Creek group in the Pilbara[11], and the Hardy formation in the Pilbara[11] falls between the 2.78-Gyr-old Mount Roe and 2.74-Gyr-old Kylena subaerial LIPs (Fig. 1). However, the most profound and permanent change occurred abruptly, coinciding with the ~2.51- to 2.45-Gyr-long period of increased mantle plume activity and subaerial volcanism during the final stages of amalgamation of Late Archaean cratons to form the first large stable continents or supercontinent[4].

The redox state of volcanic gases differs markedly between subaerial and submarine eruptions[6,17]. Volcanic gases that erupted subaerially have generally equilibrated at high temperatures and low pressures with magmas close to the fayalite–magnetite–quartz buffer. Consequently, oxidized gases (H_2O, CO_2 and SO_2) dominate. Submarine volcanoes erupt at lower temperatures and thus are more reducing[17]. Hydrothermal vent fluids equilibrate with a suite of alteration minerals at intermediate temperatures and higher pressure, and are thus also more reduced fluids with higher concentrations of H_2, CO, CH_4 and H_2S.

Holland[6] characterizes the reducing power of volcanic gases with a term f defined as:

$$f = \frac{m_{H_2} + 0.6m_{CO} + 3.6m_{CH_4} + 3m_{H_2S} - 0.4m_{CO_2}}{3.5(m_{SO_2} + m_{H_2S})} + \frac{1}{3.5}$$

modified by us to include CH_4. Here m_i represents the molal concentration of species i in hydrothermal fluids or the mole or volume fraction of i for volcanic gases, and the numbers are derived from the stoichiometries of the reactions that produce organic matter and pyrite from the volcanic gases. f values greater than 1, if representative of the global average, imply that there is more than enough reducing power to convert 20% of the CO_2 to organic C (based on the C isotope constraint) and all of the sulphur to pyrite, allowing H_2 to accumulate in the atmosphere. Alternatively, one may think of Holland's f as indicative of the reducing power of volcanic gases, which when combined with the total flux of volcanic gases gives the oxygen demand of volcanic emanations. Oxygen levels rise when the demand for oxygen falls below its supply.

The non-flux-weighted average f value for subaerial volcanic gases (including methane) is (mean $\pm$ standard error) 0.48 ± 0.14 (see Supplementary Tables 3 and 4 for data used and statistical analysis). The range is quite large, from f values below -2 (that is, insufficiently reducing to support 20% conversion of CO_2 to organic matter) to values greater than $+4$. Conceivably, the flux-weighted average could lie towards one end of this range if more- or less-oxidizing volcanoes dominated the global flux. However, most of the values for modern subaerial volcanoes fall between 0.2 and 0.7 (Fig. 3). In contrast, the range of f values for hydrothermal fluids is much smaller, and the average f of 1.04 ± 0.04 falls well above the range for most subaerial volcanoes. A two-tailed Student's t-test assuming unequal variances confirms that the sample means are different, with the probability that the means are the same being 0.0003. With the caveat that our estimate of the average subaerial f value is subject to revision based on a more complete accounting of subaerial volcanic fluxes and their redox state, the relative proportions of subaerial and submarine volcanism today cited by Holland[6] give a global f value of $\sim$0.69. This value falls well below the threshold for anoxia ($f = 1$), as one would expect given the oxygenated state of today's atmosphere.

The data and arguments presented above support the conclusion that the proportion of subaerial volcanism in the Archaean was low. This alone may have been just sufficient to create an anoxic atmosphere, given that submarine volcanoes have an f value very near 1. However, in a sulphate-free Archaean ocean[28], the H_2 concentration of hydrothermal fluids would have been up to two orders of magnitude larger[29], even though the H_2S concentration would have been similar to average vent fluids today. Using the same CO_2 concentration as Holland's average[6] (2.0×10^{-2} molal) and an H_2 concentration of 1.8×10^{-2} m (figure 1 in ref. 29) produces an f value for typical hydrothermal volcanism of the Archaean of 1.5 (CH_4 not included). In other words, there would have been at least 50% excess reducing power in Archaean submarine volcanic emissions beyond that used by organisms for reducing carbon dioxide and consumed by the reduction of volcanic SO_2. This excess hydrogen would have been available to accumulate in the atmosphere or be used by methanogens[16,30]; in either case, a reducing atmosphere free of molecular oxygen would have existed.

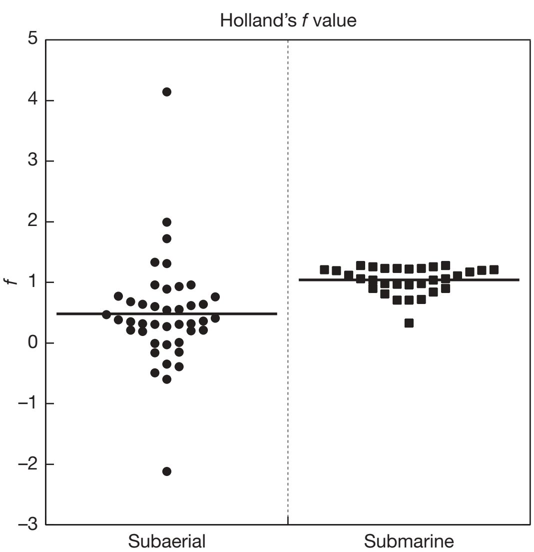

Figure 3 | The distribution of Holland's f values[6] for modern submarine and subaerial volcanoes. The calculation includes CH_4. See Supplementary Table 3 for documentation of sources. A global average of $f > 1$ is sufficiently reducing to allow H_2 accumulation in the atmosphere. $f = 1$ reduces 20% of CO_2 to organic matter and all the SO_2 to pyrite. $f = 0$ reduces 20% of CO_2 to organic carbon but no SO_2 to pyrite. $f < 0$ has insufficient reducing power to reduce 20% of CO_2 to organic carbon.

We thus propose that the rise of atmospheric oxygen was closely tied to Earth's tectonic evolution (Fig. 1). Evidence for a possible early rise to low oxygen levels between $\sim$2.92 and 2.74 Gyr ago coincides with stabilization of the Pilbara and Kaapvaal cratons and subsequent continental subaerial flood basalt volcanism, with the most intense episode of dominantly submarine mantle plume activity recorded in the Earth's history occurring 2.72–2.66 Gyr ago and resulting in a return to anoxic conditions. The abrupt switch at $\sim$2.5 Gyr ago from dominantly submarine volcanic eruptions to a mixture of submarine and subaerial eruptions similar to that of the Phanerozoic was coincident with strong evidence for the permanent establishment of atmospheric oxygen. Either cyanobacterial evolution was somehow tied to the tectonic event 2.5 Gyr ago, or more likely, cyanobacterial oxygenic photosynthesis evolved earlier, but an overwhelming volcanic sink delayed its expression in the atmosphere. As oxygen levels rose, the sink for oxygen associated with submarine volcanism was replaced by the modern weathering sink, including the weathering of subaerial volcanoes, and these sinks grew with atmospheric oxygen levels until a new atmospheric steady state was achieved that was sufficiently oxygen-rich to quench the preservation of MIF sulphur isotope effects.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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