Letter

Did mantle plume magmatism help trigger the Great Oxidation Event?

T. Jake. R. Ciborowski [a,b,*], Andrew C. Kerr [c]

[a] School of Environment and Technology, University of Brighton, Brighton BN2 4GJ, UK
[b] Earth and Ocean Sciences, School of Natural Sciences, National University of Ireland, Galway, Ireland
[c] School of Earth and Ocean Sciences, Cardiff University, Park Place, Cardiff CF10 3AT, UK

ABSTRACT

The Great Oxidation Event (GOE) represents the first sustained appearance of free oxygen in Earth's atmosphere. This fundamental event in Earth's history has been dated to approximately 2450 million years ago (Ma), that is, hundreds of millions of years after the appearance of photosynthetic cyanobacteria in the fossil record. A variety of mechanisms have been suggested to explain this time lag between the onset of photosynthesis and atmospheric oxygenation, including orogenesis, changes in the areal extent and distribution of continental shelves, the secular release of hydrogen to space, and methanogenic bacterial stress. Recently, it has been proposed that subaerial volcanism during the early Proterozoic could have provided a large pulse of sulphate to the ancient oceans, the reduction of which liberated the oxygen to drive the GOE. Here we show that the Matachewan Large Igneous Province (LIP), which is partially preserved in Scandinavia and North America, is both exactly coincident with the onset of the GOE, and of sufficient magnitude to be the source of this sulphate release. We therefore propose that the volcanism associated with the emplacement of the Matachewan LIP was a principal driver of the oxygenation of our planet.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

The Great Oxidation Event (GOE; Holland, 2002) represents the first sustained appearance of free oxygen in the atmosphere. This event which was fundamental to the evolution of complex, multicellular life on Earth (Caitling et al., 2005; Lane and Martin, 2010) occurred at ~2450 Ma with a shift from prevailing atmospheric anoxia to more oxic conditions (e.g., Lyons et al., 2014). This change is evidenced in the geological record by the absence of detrital minerals that are unstable in the presence of oxygen, in sediments younger than the Archean. These minerals are however common in older rocks (Frimmel, 2005; Rasmussen and Buick, 1999). Moreover, mass-independent fractionation (MIF) of sulphur isotopes [proposed to indicate a reducing atmosphere (Farquhar and Wing, 2003)] has not been found in rocks deposited since the earliest Proterozoic (Johnston, 2011) (Fig. 1). Indeed, it has been shown that in order to inhibit the MIF of sulphur isotopes, atmospheric oxygen must have risen to at least 1×10^{-5} present atmospheric levels at the start of the Proterozoic (e.g., Kump, 2008; Pavlov and Kasting, 2002).

Although it has long been argued that atmospheric oxygenation at 2450 Ma was driven by cyanobacterial photosynthesis (e.g, Canfield, 2005; Kopp et al., 2005), the Archean stratigraphic record contains even older evidence of Archean oxygenic photosynthesis in the form of distinct isotopic signatures (e.g., δ^{98}Mo values that are consistent with interaction with Mn oxides, and strongly negative δ^{13}C) and biomarker molecules (indicative of cyanobacterial metabolic processes) are preserved within sediments that were deposited hundreds of millions of years prior to the GOE (Planavsky et al., 2014; Rosing and Frei, 2004). Aside from these isotopic data, paleontological evidence in the form of fossilised tufted microbial mats – which in the modern era are dominated by cyanobacteria – are preserved in rocks as old as 2.72 Ga (Flannery and Walter, 2011). The time lag between the onset of photosynthesis and the GOE suggests that other mechanisms are likely to have operated ~2450 Ma to either increase the rate of oxygen production, or alternatively, inhibit the ability of the Archean sinks to remove O_2 as it was photosynthesised.

Various mechanisms have been suggested to explain the lag between the onset of photosynthesis and the GOE (see review in Kasting, 2013). For example, partial cessation of ultramafic volcanism towards the end of the Archean aeon may have caused a decrease in the flux of nickel into the oceans (Konhauser et al., 2009). Limited nickel supply could have arrested the activity of Archean methanogens leading to a decrease in the amount of atmospheric methane which would have otherwise consumed photosynthetic O_2. Alternatively, periods of continental collision and orogenesis may have been the trigger for the GOE by increasing primary productivity in the oceans through increased

* Corresponding author at: School of Environment and Technology, University of Brighton, Brighton BN2 4GJ, UK.
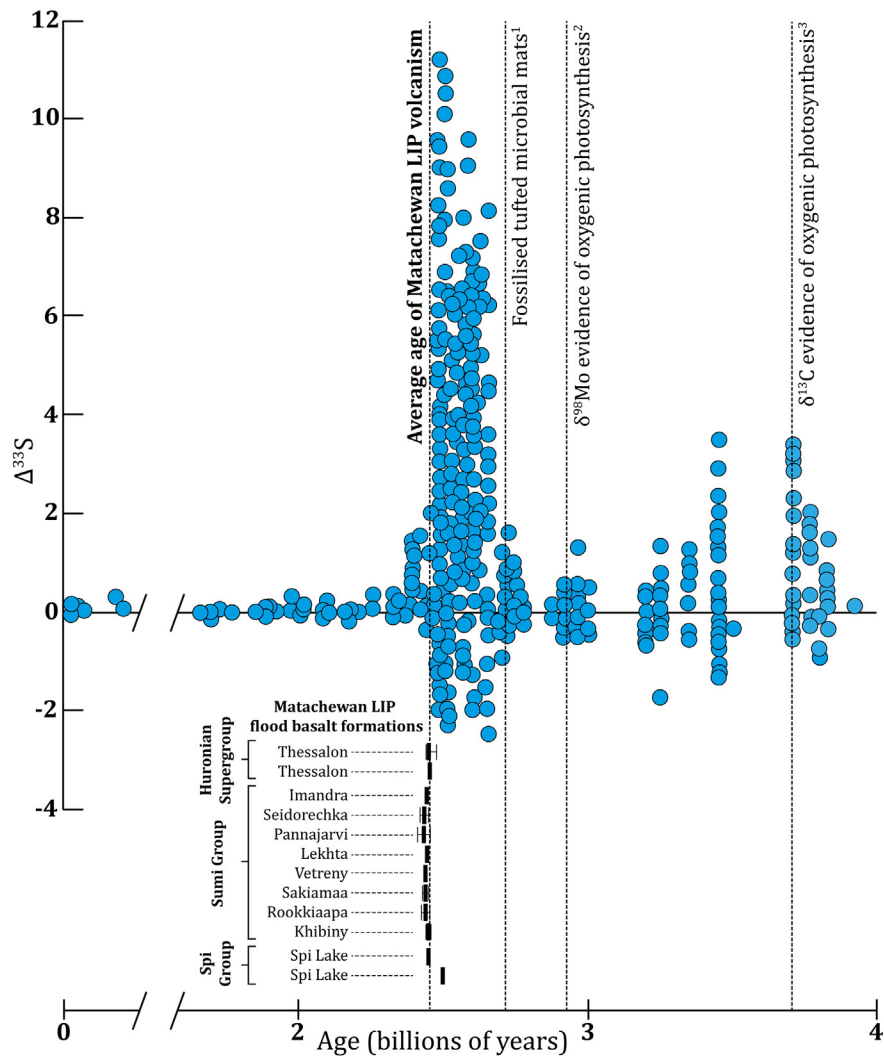   E-mail address: j.ciborowski@brighton.ac.uk (T.J.R. Ciborowski).

Fig. 1. $\Delta^{33}S$ versus age. Note the prevalence of MIF of sulphur isotopes in rocks older than 2450 Ma and absence in rocks deposited after. Also plotted are age estimates for each of the individual Matachewan LIP flood basalt formations (Table 1). $\Delta^{33}S$ data from (Johnston, 2011). Superscripts: 1 – Flannery and Walter (2011), 2 – Planavsky et al. (2014), 3 – Rosing and Frei (2004).

nutrient supply, as well as increasing organic carbon burial rates (Campbell and Allen, 2008). Other models propose that increasing the size of the early Proterozoic continental shelf seas during episodes of continental rifting promoted organic carbon burial (Lenton et al., 2004). A change in the nature of volcanic gases from more reduced compositions during the Archean to more oxidised compositions during the Proterozoic has also been suggested as a cause of the GOE (Kump and Barley, 2007). However, all these mechanisms have difficulty in explaining the apparent abruptness (see Lyons et al., 2014 for an alternative interpretation) of the change at the time of the GOE.

Alternatively, it has recently been proposed that O_2 released by the reduction of volcanogenic SO_2 (as sulphate ions in seawater) derived from Proterozoic subaerial volcanism may have driven the GOE (Gaillard et al., 2011). In this paper, we propose that the Matachewan LIP represents the main volcanic event responsible for the initial oxidation of the Earth's atmosphere. During volcanic eruptions, volatile species dissolved in the magma are released to a degree that is dictated by the confining pressure at which the eruption occurs (Gaillard et al., 2011). In modern systems, significant degassing of sulphur does not occur during subaqueous eruptions under confining pressures >100 bars, but can be almost total during subaerial eruptions (Rhodes and Vollinger, 2005). Empirically estimating the amount of sulphur

(and hence, SO_2) released by ancient volcanic eruptions can be achieved by comparing the compositions of degassed lavas with those of related (but undegassed) subsurface magmas (Thordarson and Self, 2003). Here we focus on the Kaminak dyke swarm, a key component of the Matachewan LIP, preserved in the Central Hearne Supracrustal Belt, Nunavut, Canada (Sandeman and Ryan, 2008).

The Matachewan LIP is a reconstructed magmatic system of dyke swarms, layered intrusions, and the eroded remains of one of the largest continental flood basalt provinces in the geological record, fragments of which are now preserved in North America and Scandinavia (Fig. 2) (Ciborowski et al., 2015). The radiating geometry of the dyke swarms and high volumes of mafic rock preserved in this LIP imply a mantle plume origin for the magmatism (Ernst and Buchan, 2002). U—Pb ages for the different igneous suites show that magmatism began with the intrusion of the dyke swarms and layered intrusions ~2495 Ma (Vogel et al., 1998). Following the establishment of this crustal magmatic system, continental flood basalts were erupted on the Karelia, Kola, Hearne, and Superior cratons. Crucially, the preserved flood basalts record eruptive ages of between ~2432 and ~2453 Ma (Ketchum et al., 2013; Melezhik, 2006) with an average age of 2442 Ma (Table 1; Fig. 1) – indistinguishable from age estimates of the GOE (Johnston, 2011). Given the remarkably coeval nature of the GOE and Matachewan
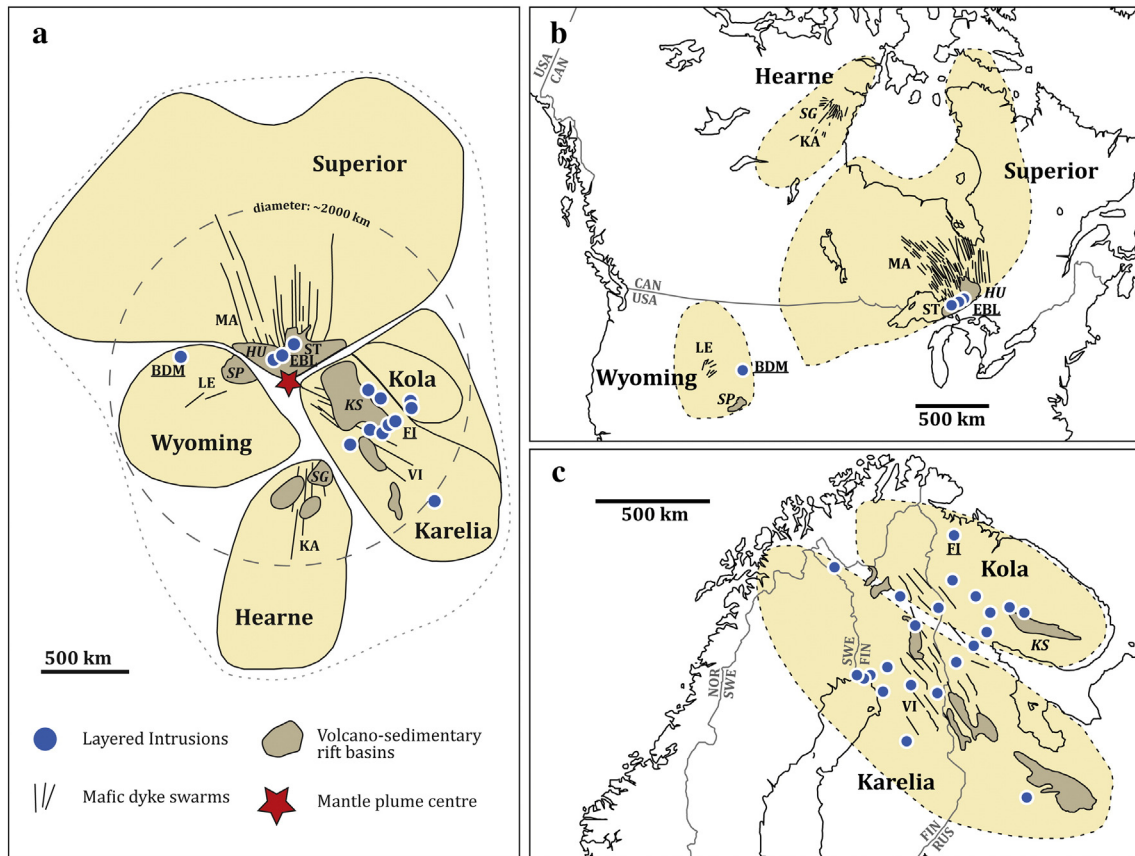
Fig. 2. (a) Early Proterozoic Matachewan LIP reconstruction (Modified after Bleeker and Ernst, 2006) and the Matachewan LIP's constituent suites' present-day distribution (b) and (c). When reconstructed to their inferred primary distribution, the composite radiating dyke swarm defines a mantle plume locus, melting at which triggered the emplacement of the LIP. Mafic dyke swarms: MA – Matachewan, VI – Viianki, LE – Leopard, KA – Kaminak, ST – Streich; Volcano-sedimentary rift basins: HU – Huronian Supergoup, KS – Karelia Supergroup, SP Snowy Pass Supergroup, SG – Spi Group; Layered Intrusions: EBL – East Bull Lake Suite, FI – Fennoscandian Intrusions, BDM – Blue Draw Metagabbro.

LIP volcanism, especially in light of previous studies that have demonstrated the ability of LIPs to help drive fundamental change in the biosphere (e.g., Courtillot et al., 1986; Renne et al., 1995), the potential of a causal link between the Matachewan LIP and the GOE must be explored.

The Kaminak dyke swarm is made up of hundreds of NNE trending gabbroic dykes, which range in thickness from 1 to 40 m. Stratigraphically above, and orientated parallel to the strike of, the Kaminak dykes is the 8 km^2 Spi Basin which contains a 75–100 m thick sequence of basaltic

lava flows and intercalated sediments. These basalts have identical trace element (Fig. 3) and radiogenic isotopic compositions to the Kaminak dykes and are interpreted to be their eruptive equivalents, emplaced into the basin during a period of crustal extension (Sandeman and Ryan, 2008). The Kaminak dykes and the cogenetic Spi Basin lavas are

Table 1
Summary of cited U—Pb ages for constituent Matachewan LIP Flood Basalt Provinces. Abbreviations: bad – baddeleyite, zir – zircon.

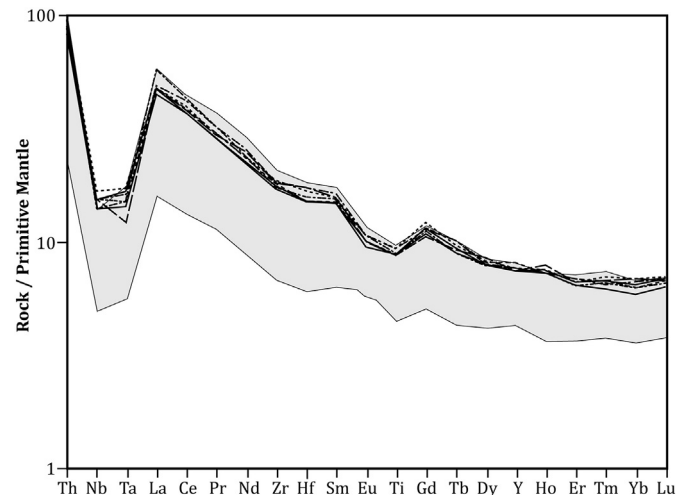| Flood Basalt Province	Age (Ma)	Analysis type	Reference
Huronian Supergroup			
Thessalon Formation	2450^{+25}_{-10}	zir	Krogh et al. (1984)
	2453 ± 3	zir	Ketchum et al. (2013)
Karelia Supergroup			
Seidorechka Formation			
Seidorechka	2434 ± 15	bad + zir	Bayanova and Balashov (1995)
Imandra	2442 ± 2	bad	Amelin et al. (1995)
Paanajärvi	2432 ± 22	zir	Buiko et al. (1995)
Lekhta	2443 ± 5	zir	Levchenkov et al. (1994)
Vetreny Belt	2437 ± 3	zir	Puchtel et al. (1997)
Sakiamaa	2438 ± 11	zir	Räsänen and Huhma (2001)
Rookkiaapa	2438 ± 14	zir	Manninen et al. (2001)
Khibiny	2448 ± 8	zir	Chashchin et al. (2008)
Spi Group			
Spi Lake Formation	2450 ± 2	bad	Heaman (1994)
	2498 ± 1	bad	Sandeman et al. (2013)

Fig. 3. Primitive Mantle-normalised trace element diagram showing the compositions of the Spi Group basalts (black lines) and the cogenetic Kaminak dykes (grey field). The Spi Group data (n = 7) are from Sandeman and Ryan (2008) while the Kaminak dyke data (n = 57) are from Ciborowski et al. (2015). Primitive Mantle normalising values from McDonough and Sun (1995).
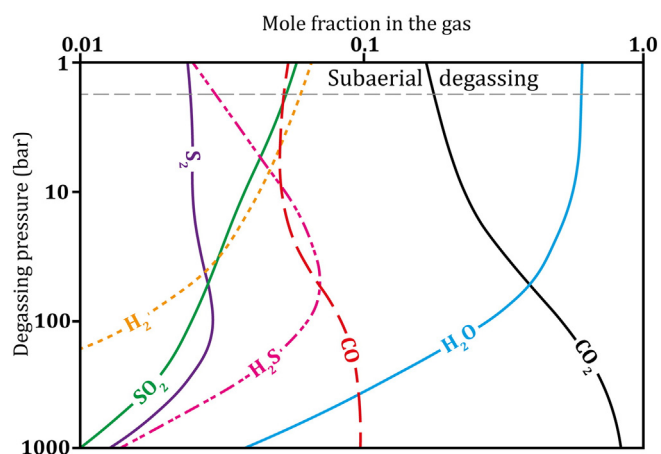
Fig. 4. Calculated compositions of volcanic gases as a function of pressure (Gaillard et al., 2011). During subaerial eruptions at very low degassing pressures, tholeiitic lavas lose sulphur as a mixture of SO_2, H_2S, and S_2.

therefore an ideal system for investigating the amount of sulphur released by the Matachewan LIP.

2. Results

Using a thickness of 75 m for the Spi Basin lavas across the 8 km^2 basin and an average basaltic density of 2900 kg m^{-3}, the mass of lava can be estimated as 1.74×10^{12} kg. Whole rock data (15 samples) for the Kaminak dykes and Spi Basin lavas, on average, show that they contain 1036 and 710 ppm sulphur, respectively (Sandeman and Ryan, 2008), which implies that the 326 ppm deficit was lost to the atmosphere during degassing of the erupted lava. Using established methods used for calculating volatile release in modern eruptions (Thordarson and Self, 2003), the sulphur difference between the degassed lavas and undegassed dykes can be calculated to represent an absolute flux of 5.67×10^{10} kg of sulphur released into the Archean–early Proterozoic atmosphere during the eruption of the Spi Basin lavas (1).

$$(0.1036\text{–}0.0710) \times \left(1.74 \times 10^{12} \text{kg}\right) = 5.67 \times 10^{10} \text{kg} \quad (1)$$

The remaining Matachewan LIP flood basalts are preserved in the Huronian Supergroup (southern Ontario) and Sumi Group (Kola-Kaleria), the volcanic portions of which have average thicknesses of 1200 and 2500 m, respectively (Ketchum et al., 2013; Melezhik, 2006). Based on the presently exposed areas of these two groups, a minimum quantity of lava erupted as part of the Matachewan LIP may be estimated to be ~34,000 km^3 or ~ 9.91×10^{16} kg of basalt. If we assume that the Huronian Supergroup and Sumi Group basalts emitted sulphur in the same way as the coeval (and potentially cogenetic) Spi Basin lavas, the Matachewan LIP flood basalts would have released ~3.23×10^{15} kg of S into the early Proterozoic atmosphere. It is critical to note that these estimates of lava volumes are based on current eroded remnants of the province which, in comparison to modern, less-eroded LIPs, are significantly smaller. If instead, we were to assume that the original Matachewan LIP was comparable in size to Phanerozoic analogues (as is suggested by the spatial distribution of the radiating dyke swarms of the province), then the estimates presented here should be increased by at least an order of magnitude.

During volcanic eruptions, sulphur is not emitted from lava in its native state and is instead lost as a mixture of S_2, H_2S, and SO_2. The relative proportions of these species vary as a function of pressure (Gaillard et al., 2011). The lack of pillow lavas within, and the preservation of regolith below, the Spi Basin, Huronian Supergroup, and Sumi Group lavas suggest that they were erupted subaerially under normal atmospheric
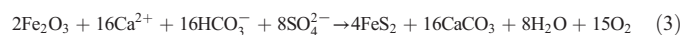
pressures (Ketchum et al., 2013; Melezhik, 2006; Sandeman and Ryan, 2008). Under such conditions, tholeiitic-basalt eruptions emit SO_2, S_2, and H_2S in a molar ratio of approximately 2.5:1:1 (Fig. 4) (Gaillard et al., 2011). Thus, for every mole of sulphur emitted by volcanic eruptions, 0.544 moles of SO_2 and 0.222 and 0.234 moles each of H_2S and S_2 are released. By converting the 3.23×10^{15} kg of sulphur released by the Matachewan lavas into moles of S (1.01×10^{17}) and using the eruptive molar ratios noted above, the number of moles of SO_2, S_2, and H_2S emitted to the atmosphere during the eruptions of the Matachewan LIP lavas can be estimated to be at least 5.49×10^{16}, 2.24×10^{16}, and 2.36×10^{16}, respectively.
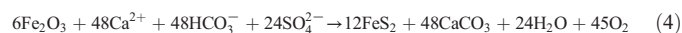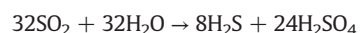
3. Discussion

Recent work by Gaillard et al. (2011) suggests that decomposition of the SO_2 released by Paleoproterozoic subaerial volcanism (like that which characterised the Matachewan LIP) would have resulted in significant amounts of sulphuric acid (H_2SO_4) forming (2) in the atmosphere (Symonds et al., 2001):

$$4SO_2 + 4H_2O \rightarrow H_2S + 3H_2SO_4 \quad (2)$$

Dissolution of this H_2SO_4 in the Paleoproterozoic oceans produced sulphate (SO_4^{2-}) ions which would have been metabolised by sulphate-reducing bacteria to produce sedimentary pyrite (FeS_2) (Berner and Canfield, 1989; Kasting, 2013). The net result of sulphate reduction and subsequent pyrite formation (and burial) is an increase in atmospheric O_2 that can be summarised (3) by the following reaction (Lyons and Gill, 2010):

$$2Fe_2O_3 + 16Ca^{2+} + 16HCO_3^- + 8SO_4^{2-} \rightarrow 4FeS_2 + 16CaCO_3 + 8H_2O + 15O_2 \quad (3)$$

Balancing the two reactions presented above in terms of SO_4^{2-} shows that for every 32 moles of SO_2 released into the atmosphere by subaerial volcanism, 45 moles of O_2 may be produced via sulphate reduction in the oceans (4).

$$32SO_2 + 32H_2O \rightarrow 8H_2S + 24H_2SO_4$$

$$6Fe_2O_3 + 48Ca^{2+} + 48HCO_3^- + 24SO_4^{2-} \rightarrow 12FeS_2 + 48CaCO_3 + 24H_2O + 45O_2 \quad (4)$$

Using the 5.49×10^{16} moles of SO_2 estimated to have been released by the Matachewan LIP, we can calculate that the number of moles of O_2 produced by these reactions would have 7.72×10^{16}. This equates to a mass of O_2 of 2.47×10^{15} kg. The mass of the modern atmosphere is approximately 5.15×10^{18} kg (Trenberth and Smith, 2005) of which 23% (1.18×10^{18} kg) is O_2. Thus, the eruption of the Matachewan LIP flood basalts may have released an amount of O_2 equivalent to ~0.2% of that in the present-day atmosphere. This value is significant as it represents a potential oxygen input, greater in magnitude than that required to arrest the MIF of sulphur observed in the Archean geological record before the GOE (Kump, 2008; Pavlov and Kasting, 2002).

In comparison to the largest lava flow in recorded history – the 1783–1784 Laki eruption (15.3 km^3) – where the SO_2 released was similarly calculated to have been 1.22×10^{11} kg (Thordarson and Self, 2003), the Matachewan LIP is a truly enormous eruption. More significantly, the estimated eruptive volumes of the Matachewan LIP flood basalts are calculated from the size of current exposures and thus represent an absolute minimum estimate. Given the ages and post-intrusion tectonic histories of the constituent volcanic provinces, the modern day exposures represent only a small fraction of the original erupted Matachewan LIP flood basalt volume (Ernst and Buchan, 2002). Thus, the calculations above may significantly underestimate the actual amount of SO_2 released into the early Proterozoic atmosphere via the eruption of the Matachewan LIP. Indeed, if we were to assume that the original volume of the Matachewan LIP prior to its erosion was similar to that of the Siberian Traps (~4×10^6 km^3; i.e., ~120 times larger) see

Maysatis, 1983), then the mass of oxygen released via the mechanisms explained above could have been up to 2.89×10^{17} kg – equivalent to ~20% of that in the present-day atmosphere.

It is important to note that the calculations above are underpinned by several assumptions. Firstly, estimating eruptive rates and associated fluxes of gas species to the atmosphere is difficult. This is largely the result of (often poor) temporal constraints on regions of the Matachewan LIP, with many of the constituent flood basalt provinces (currently) being constrained by one – very occasionally two – U—Pb radiometric ages. That said, the age of the Matachewan LIP volcanic rocks hosted within the Huronian Supergroup is bracketed by the ~2491 Ma Agnew lake intrusion, upon which the Huronian Supergroup sits unconformably (Vogel et al., 1998), and the ~2450 Ma Copper Cliff Rhyolite (Ketchum et al., 2013) preserved at the top of the volcanic sequence. Thus, the absolute maximum lifespan of the Matachewan LIP flood basalt province can be estimated to be ~40 myr, though is likely to be much less than this (Fig. 1). Without further geochronological constraints, the calculation of atmospheric fluxes is necessarily speculative.

The second assumption comes from the fact that we use sulphur analyses from the relatively minor Spi Basin lavas to constrain the SO_2 release of the LIP as a whole, despite the potential for variation across the LIP. Further, we assume that all of the SO_2 released by the volcanism is reduced in the oceans during sedimentary pyrite formation, and that the O_2 produced during sulphate reduction is free to accumulate in the atmosphere. This latter assumption is questionable as, aside from the SO_2 released by the Matachewan LIP magmatism, sizeable amounts of other reductants (e.g., CO, H_2 H_2S, and S_2) that could have consumed a portion of the O_2 produced through sulphate reduction (5, 6, 7, 8) would also have been released (Fig. 4; Gaillard et al., 2011).

$$2CO + O_2 \rightarrow 2CO_2 \tag{5}$$

$$2H_2 + O_2 \rightarrow 2H_2O \tag{6}$$

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2 \tag{7}$$

$$S_2 + O_2 \rightarrow 2SO_2 \tag{8}$$

However, even when we factor in the O_2 consumption resulting from the release of the reductants listed above (the number of moles of which can be calculated using the relative proportions supplied in Fig. 2), as well the effects of reseeding of the atmosphere with the SO_2 produced via the oxidation of volcanogenic H_2S and S_2 (Eqs. (7) and (8)), the overall effect is still a significantly positive increase (6.00×10^{16} moles) in the amount of O_2 delivered to the Paleoproterozoic atmosphere. If we convert this number of moles of O_2 into kg, we can calculate a mass of O_2 produced by the Matachewan LIP eruptions of ~1.92×10^{15} kg.

Again, using Trenberth and Smith's (2005) estimate of the mass of the modern atmosphere (5.15×10^{18} kg) of which 23% (1.18×10^{18} kg) is O_2 and assuming that the Proterozoic atmosphere was not significantly different in terms of mass, we can see that the bulk O_2 addition caused by the eruption of the Matachewan LIP equates to an O_2 concentration equal to 1.62×10^{-3} that of present atmospheric levels – i.e., sufficient to inhibit the MIF of sulphur isotopes observed in sediments deposited during the Archean aeon (Kump, 2008; Pavlov and Kasting, 2002). Lastly, the effects of oxidative weathering of the continents (Campbell and Allen, 2008), as well as potential changes in methanogen production (Konhauser et al., 2009) following the erosion of the Matachewan LIP basalts, are not accounted for in our model.

Despite the potential buffering effects of these last two processes and the very conservative estimate of magmatic volumes, we must also remember that the Archean–Paleoproterozoic transition heralds the first emergence of the continents from the Archean oceans (Flament et al., 2008). One of the myriad effects of this fundamental change in the Earth system is that the composition of volcanic gases changed from more reducing to more oxidising as eruptions became more subaerial in nature (Gaillard et al., 2011; Kump and Barley, 2007).

4. Conclusion

Against this backdrop of global change, the Matachewan LIP represents one of the first, truly massive igneous events that occurs after the emergence of the continents and this shift in volcanic gas chemistry. Given the contemporaneous nature of the Matachewan LIP with the GOE, and the calculations detailed above, there is a strong case for the Matachewan LIP to be a principal driver of the GOE. The O_2 released during reduction of volcanogenic SO_2 in the oceans represents an input of sufficient magnitude to inhibit the MIF of sulphur and ultimately drive the oxygenation of Earth's atmosphere.

If valid, this mechanism for the initiation of the GOE will require a re-evaluation of these enormous magmatic systems, not just as drivers of biotic stress (Sobolev et al., 2011), but also to acknowledge their apparent ability to enable, and to drive, the evolution of life into the complex, and multicellular forms we see today.

Acknowledgments

Appendix A. Supplementary data

Attached is a .doc file which details the calculations described in the discussion. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.lithos.2015.12.017.

References

Amelin, Y.V., Heaman, L.M., Semenov, V.S., 1995. U–Pb geochronology of layered mafic intrusions in the eastern Baltic Shield: implications for the timing and duration of Paleoproterozoic continental rifting. Precambrian Research 75, 31–46.

Bayanova, T., Balashov, Y., 1995. Geochronology of Palaeoproterozoic layered intrusions and volcanites of the Baltic Shield. Norges Geologiske Undersökelse, Special Paper 7, 75–80.

Berner, R.A., Canfield, D.E., 1989. A new model for atmospheric oxygen over Phanerozoic time. American Journal of Science 289, 333–361.

Bleeker, W., Ernst, R.E., 2006. Short-lived mantle generated magmatic events and their dike swarms: the key unlocking. In: Hanski, E., Mertanen, S., Rämö, T., Vuollo, J. (Eds.), Dike Swarms: Time Markers of Crustal Evolution. Earth's paleogeographic record back to 2.6 Ga.Taylor & Francis/Balkema, Leiden, pp. 3–26

Buiko, A., Levchenkov, O., Turchenko, S., Drubetskoi, E., 1995. Geology and isotopic dating of the early Proterozoic Sumian-Sariolian Complex in northern Karelia (Paanajärvi-Tsipringa structure). Stratigraphy and Geological Correlation 3, 16–30.

Caitling, D.C., Clein, C.R., Zahnle, K.J., McKay, C.P., 2005. Why O_2 is required by complex life on habitable planets and the concept of planetary "oxygenation time". Astrobiology 5, 415–438.

Campbell, I.H., Allen, C.M., 2008. Formation of supercontinents linked to increases in atmospheric oxygen. Nature Geoscience 1, 554–558.

Canfield, D.E., 2005. The early history of atmospheric oxygen: homage to Robert M Garrels. Annual Review of Earth and Planetary Sciences 33, 1–36.

Chashchin, V., Bayanova, T., Levkovich, N., 2008. Volcanoplutonic association of the early-stage evolution of the Imandra-Varzuga rift zone, Kola Peninsula, Russia: geological, petrogeochemical, and isotope-geochronological data. Petrology 16, 279–298.

Ciborowski, T.J.R., Kerr, A.C., Ernst, R.E., McDonald, I., Minifie, M.J., Harlan, S.S., Millar, I.L., 2015. The Early Proterozoic Matachewan large igneous province: geochemistry, petrogenesis, and implications for Earth evolution. Journal of Petrology 56, 1459–1494.

Courtillot, V., Besse, J., Vandamme, D., Montigny, R., Jaeger, J.-J., Cappetta, H., 1986. Deccan flood basalts at the Cretaceous/Tertiary boundary? Earth and Planetary Science Letters 80, 361–374.

Ernst, R.E., Buchan, K.L., 2002. Maximum size and distribution in time and space of mantle plumes: evidence from large igneous provinces. Journal of Geodynamics 34, 309–342.

Farquhar, J., Wing, B.A., 2003. Multiple sulfur isotopes and the evolution of the atmosphere. Earth and Planetary Science Letters 213, 1–13.

Flament, N., Coltice, N., Rey, P.F., 2008. A case for late-Archaean continental emergence from thermal evolution models and hypsometry. Earth and Planetary Science Letters 275, 326–336.

Flannery, D.T., Walter, M.R., 2011. Archean tufted microbial mats and the Great Oxidation Event: new insights into an ancient problem. Australian Journal of Earth Sciences 59, 1–11.

Frimmel, H.E., 2005. Archaean atmospheric evolution: evidence from the Witwatersrand gold fields, South Africa. Earth Science Reviews 70, 1–46.

Gaillard, F., Scaillet, B., Arndt, N.T., 2011. Atmospheric oxygenation caused by a change in volcanic degassing pressure. Nature 478, 229–232.

Heaman, L.M., 1994. 2.45 Ga global mafic magmatism: Earth's oldest superplume? Eighth International Conference on Geochronology, Cosmochronology, and Isotope Geology; Program with Abstracts, U.S. Geological Survey Circular 1107, p. 132

Holland, H.D., 2002. Volcanic gases, black smokers, and the Great Oxidation Event. Geochimica et Cosmochimica Acta 66, 3811–3826.

Johnston, D.T., 2011. Multiple sulfur isotopes and the evolution of Earth's surface sulfur cycle. Earth Science Reviews 106, 161–183.

Kasting, J.F., 2013. What caused the rise of atmospheric O_2? Chemical Geology 362, 13–25.

Ketchum, K.Y., Heaman, L.M., Bennett, G., Hughes, D.J., 2013. Age, petrogenesis and tectonic setting of the Thessalon volcanic rocks, Huronian Supergroup, Canada. Precambrian Research 233, 144–172.

Konhauser, K.O., Pecoits, E., Lalonde, S.V., Papineau, D., Nisbet, E.G., Barley, M.E., Arndt, N.T., Zahnle, K., Kamber, B.S., 2009. Oceanic nickel depletion and a methanogen famine before the Great Oxidation Event. Nature 458, 750–753.

Kopp, R.E., Kirschvink, J.L., Hilburn, I.A., Nash, C.Z., 2005. The Paleoproterozoic snowball Earth: a climate disaster triggered by the evolution of oxygenic photosynthesis. Proceedings of the National Academy of Sciences of the United States of America 102, 11131–11136.

Krogh, T.E., Davis, D.W., Corfu, F., 1984. Precise U–Pb zircon and baddelyite ages for the Sudbury area. In: Pye, E.G., Naldrett, A.J., Giblin, P.E. (Eds.), The geology and ore deposits of the Sudbury structure Special vol. 1. Ontario Geological Survey, pp. 431–446.

Kump, L.R., 2008. The rise of atmospheric oxygen. Nature 451, 277–278.

Kump, L.R., Barley, M.E., 2007. Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. Nature 448, 1033–1036.

Lane, N., Martin, W., 2010. The energetics of genome complexity. Nature 467, 929–934.

Lenton, T.M., Schellnhuber, H.J., Szathmary, E., 2004. Climbing the co-evolution ladder. Nature 431, 913–913.

Levchenkov, O., Nikolaev, A., Bogomolov, E., Yakovleva, S., 1994. U–Pb ages of Sumian acid magmatic rocks in northern Karelia. Stratigraphy and Geological Correlation 2, 3–9.

Lyons, T.W., Gill, B.C., 2010. Ancient sulfur cycling and oxygenation of the early biosphere. Elements 6, 93–99.

Lyons, T.W., Planavsky, N.J., Reinhard, C.T., 2014. The rise of oxygen in the early ocean and atmosphere. Nature 506, 307–315.

Manninen, T., Pihlaja, P., Huhma, H., 2001. U–Pb geochronology of the Peurasuvanto area, northern Finland. In: Vaasjoki, M. (Ed.), Radiometric Age Determinations from Finnish Lapland and Their Bearing on the Timing of Precambrian Volcano-Sedimentary Sequences. Geological Survey of Finland, Special Paper 33, pp. 189–200.

Maysatis, V.L., 1983. Triassic and Permian volcanism of Siberia; problem of dynamic reconstruction. Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva 112, 412–425.

McDonough, W.F., Sun, S.S., 1995. The composition of the Earth. Chemical Geology 120, 223–253.

Melezhik, V.A., 2006. Multiple causes of Earth's earliest global glaciation. Terra Nova 18, 130–137.

Pavlov, A.A., Kasting, J.F., 2002. Mass-independent fractionation of sulfur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. Astrobiology 2, 27–41.

Planavsky, N.J., Asael, D., Hofmann, A., Reinhard, C.T., Lalonde, S.V., Knudsen, A., Wang, X., Ossa Ossa, F., Pecoits, E., Smith, A.J.B., Beukes, N.J., Bekker, A., Johnson, T.M., Konhauser, K.O., Lyons, T.W., Rouxel, O.J., 2014. Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event. Nature Geoscience 7, 283–286.

Puchtel, I.S., Haase, K.M., Hofmann, A.W., Chauvel, C., Kulikov, V.S., Garbe-Schönberg, C.D., Nemchin, A.A., 1997. Petrology and geochemistry of crustally contaminated komatiitic basalts from the Vetreny Belt, southeastern Baltic Shield: evidence for an early Proterozoic mantle plume beneath rifted Archean continental lithosphere. Geochimica et Cosmochimica Acta 61, 1205–1222.

Räsänen, J., Huhma, H., 2001. U–Pb datings in the Sodankylä schist area of the Central Lapland Greenstone Belt. In: Vaasjoki, M. (Ed.), Radiometric Age Determinations from Finnish Lapland and Their Bearing on the Timing of Precambrian Volcano-Sedimentary Sequences. Geological Survey of Finland, Special Paper 33, pp. 153–188.

Rasmussen, B., Buick, R., 1999. Redox state of the Archean atmosphere: evidence from detrital heavy minerals in ca. 3250–2750 Ma sandstones from the Pilbara Craton, Australia. Geology 27, 115–118.

Renne, P.R., Black, M.T., Zichao, Z., Richards, M.A., Basu, A.R., 1995. Synchrony and causal relations between Permian–Triassic boundary crises and Siberian flood volcanism. Science 269, 1413–1416.

Rhodes, J.M., Vollinger, M.J., 2005. Ferric/ferrous ratios in 1984 Mauna Loa lavas: a contribution to understanding the oxidation state of Hawaiian magmas. Contributions to Mineralogy and Petrology 149, 666–674.

Rosing, M.T., Frei, R., 2004. U-rich Archaean sea-floor sediments from Greenland – indications of > 3700 Ma oxygenic photosynthesis. Earth and Planetary Science Letters 217, 237–244.

Sandeman, H.A., Ryan, J.J., 2008. The Spi Lake Formation of the central Hearne domain, western Churchill Province, Canada: an axial intracratonic continental tholeiite trough above the cogenetic Kaminak dyke swarm. Canadian Journal of Earth Sciences 45, 745–767.

Sandeman, H.A., Heaman, L.M., LeCheminant, A.N., 2013. The Paleoproterozoic Kaminak dykes, Hearne craton, western Churchill Province, Nunavut, Canada: Preliminary constraints on their age and petrogenesis. Precambrian Research 232, 119–139.

Sobolev, S.V., Sobolev, A.V., Kuzmin, D.V., Krivolutskaya, N.A., Petrunin, A.G., Arndt, N.T., Radko, V.A., Vasiliev, Y.R., 2011. Linking mantle plumes, large igneous provinces and environmental catastrophes. Nature 477, 312–316.

Symonds, R.B., Gerlach, T.M., Reed, M.H., 2001. Magmatic gas scrubbing: implications for volcano monitoring. Journal of Volcanology and Geothermal Research 108, 303–341.

Thordarson, T., Self, S., 2003. Atmospheric and environmental effects of the 1783–1784 Laki eruption: a review and reassessment. Journal of Geophysical Research 108, 7–29.

Trenberth, K.E., Smith, L., 2005. The mass of the atmosphere: a constraint on global analyses. Journal of Climate 18, 864–875.

Vogel, D.C., James, R.S., Keays, R.R., 1998. The early tectono-magmatic evolution of the Southern Province: implications from the Agnew Intrusion, central Ontario, Canada. Canadian Journal of Earth Sciences 35, 854–870.