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How Large Igneous Provinces affect global climate, sometimes cause mass extinctions, and represent natural markers in the geological record



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ABSTRACT

Large Igneous Provinces (LIPs) can have a significant global climatic effect as monitored by sedimentary trace and isotopic compositions that record paleo-seawater/atmosphere variations. Improved U-Pb dating (with better than 0.1 Myr resolution) for several LIPs is confirming a long-proposed mass extinction-LIP link. The most dramatic climatic effect is global warming due to greenhouse-gases from LIPs. Subsequent cooling (and even global glaciations) can be caused by CO₂ drawdown through weathering of LIP-related basalts, and/or by sulphate aerosols. Additional kill mechanisms that can be associated with LIPs include oceanic anoxia, ocean acidification, sea level changes, toxic metal input, essential nutrient decrease, producing a complex web of catastrophic environmental effects. Notably, the size of a LIP is not the only important factor in contributuing to environmental impact. Of particular significance are the rate of effusion, and the abundance of LIP-produced pyroclastic material and volatile fluxes that reach the stratosphere. While flood basalt degassing (CO₂, SO₂, halogens) is important (and is also from associated silicic volcanism), a significant amount of these gases are released from volatile-rich sedimentary rocks (e.g. evaporites and coal horizons) heated by the intrusive component of LIPs. Feedbacks are important, such as global warming leading to destabilization of clathrates, consequent release of further greenhouse gases, and greater global warming. In the broadest sense LIPs can affect (or even induce) shifts between Icehouse, Greenhouse and Hothouse climatic states. However, the specific effects, their severity, and their time sequencing is specific to each LIP. Based on the robust array of environmental effects due to LIPs, as demonstrated in the Phanerozoic record, it is suggested that LIP events represent useful time markers in the Precambrian Era as proxies for some significant global environmental changes that are preserved in the sedimentary record.

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1. Introduction

The distribution of life through the Phanerozoic and in the Proterozoic is highly discontinuous, primarily driven by environmental changes. The most dramatic and sudden environmental changes are associated with mass extinction events; these define many of the boundaries in the Phanerozoic biostratigraphic time scale (e.g. Gradstein et al., 2012a, 2012b; Ogg et al., 2008, 2016). Less extreme environmental changes and minor extinction events are also recognized by excursions in isotopic proxies for the composition of seawater and atmosphere, in the timing of anoxia events, and by sea-level changes, all reflected in the sedimentary record. This is a fast-evolving vibrant field of research that is increasingly revealing the pivotal role of LIPs in environmental changes, particularly those that are abrupt and of short

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duration (on the scale of a few million years). In contrast, those broad 10s to 100s of Myr changes recorded in sedimentary rocks are more likely linked to plate-boundary processes. Environmental changes can also be linked to other macro-properties such as changes in solar luminosity, Earth's orbit, and perhaps in the Earth's magnetic field, and due to True Polar Wander (e.g. Van Der Meer et al., 2014; Torsvik and Cocks, 2016). Herein we provide an overview of the environmental impacts of LIPs, and their role as catalysts for faunal and floral collapse and extinction events. Given the robust link that is becoming increasing evident between LIPs and abrupt global climatic change, a final section addresses the utility of LIPs as natural time markers in Precambrian time, where they represent proxies for 'golden spikes' in the sedimentary record that mark key natural boundaries in Earth history.

1.1. Large Igneous Provinces (LIPs)

Large Igneous Provinces (LIPs) represent large volume (>0.1 Mkm³; frequently above >1 Mkm³), mainly mafic (-ultramafic) magmatic

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events of intraplate affinity, that occur in both continental and oceanic settings, and are typically of short duration (<5 Myr) or consist of multiple short pulses over a maximum of a few 10s of Myr (Coffin and Eldholm, 1994, 2005; Bryan and Ernst, 2008; Bryan and Ferrari, 2013; Ernst, 2014 and references therein; cf. Sheth, 2007). They comprise volcanic packages (flood basalts), and a plumbing system of dyke swarms, sill complexes, layered intrusions, and a crustal underplate. LIPs can also be associated with silicic magmatism (including dominantly silicic events termed Silicic LIPs, or SLIPs, sometimes including so-called super-eruptions), carbonatites and kimberlites. LIPs occur at a variable rate that averages approximately every 20–30 Myr but with possible peaks associated with supercontinent breakup, back at least to 2.5 Ga (Figs. 1 and 2).The rate of LIP occurrence in the Archean is less certain due to its poorer preservation (Ernst, 2014).

LIPs are systematically linked to continental breakup (or attempted breakup) events, ore deposits of a variety of commodity types (Ernst and Jowitt, 2013), can have an influence on hydrocarbon and aquifers (Ernst, 2014; Jowitt and Ernst, 2016), and in the context of this paper,

on global climate change including extinction events (Ernst, 2014). The origin of LIPs has been controversial with a range of mechanisms proposed including: lithospheric delamination, rift related decompression melting, and edge convection (e.g. King and Anderson, 1998; Coffin and Eldholm, 1994, 2005; Foulger, 2007, 2012; Ernst, 2014). However, more accurate age dating (emphasizing the short duration of many of these huge events), the presence of giant radiating mafic dyke swarms, seismic tomography, and compositional data for elevated mantle potential temperatures provide a strong case for a LIP link with mantle plumes whose buoyancy is mainly thermal (e.g. Campbell, 2005; Ernst, 2014 and references therein). A recent paper by Wang et al. (2016) demonstrates a higher rate of water content (1-2 wt%) in the primary magmas and trace element compositions consistent with water-flux contribution to melting for several Phanerozoic LIPs (such as the 251 Ma Siberian Traps, 201 Ma Central Atlantic Magmatic Province (CAMP), 66 Ma Deccan, and 16 Ma Columbia River), suggesting a model in which an upwelling deep mantle plume interacts with subduction-transported water at the mid-mantle boundary.



Fig. 1. Part a-e. Generalized distribution of LIPs and interpreted LIP fragments through time, back to 2.5 Ga (updated from Ernst, 2014). Numbers are in Ga. Selected associated silicic LIPs (SLIPs) are shown (i.e. 0.32–0.28 Ga Kennedy-Connors-Auburn, 0.04 Ga Sierra Madre Occidental and 0.12 Whitsunday. Maps are in Robinson Projection.



Fig. 1 (continued).

1.2. Global extinction events and other environmental changes

As is well established there are repeated catastrophic changes in fauna and flora in the Phanerozoic Era (Fig. 3). There are five major extinctions (the so called "Big Five"; end-Cretaceous (66 Ma; 75% of all species lost) end-Triassic (201 Ma; 80% of species lost), end-Permian (251 Ma; 95% of species lost), end-Devonian (~375 Ma; 75% of species lost) and end-Ordovician (444 Ma; 85% of species lost), (e.g. Raup and Sepkoski, 1982; Sepkoski, 1986; Hallam and Wignall, 1997; Bambach, 2006; Whiteside and Grice, 2016) and a number of minor extinctions in which smaller percentages of life were wiped out (as measured at the family, species or genus level and dominantly in marine or terrestrial settings, or both). Accompanying these dramatic changes in fauna and flora are also rapid shifts in stable isotopes such as Sr, C, O, S, Os, Mo, Cr, Li, U, and other compositional parameters such as Hg/TOC, in the sedimentary record that are proxies for rapid changes in seawater

and atmosphere composition (Kendall et al., 2009; Montoya-Pino et al., 2010; Misra and Froelich, 2012; Cole et al., 2016; Goldberg et al., 2016; Holmden et al., 2016), and for which, in many cases, LIP can have an influence, as outlined below.

2. Links between LIPs and global extinction events

The temporal link between LIPs and extinction events appears robust (Fig. 3). Many major, and some minor, LIP events occur within several million years or less of global extinctions (e.g. Stothers, 1993; Courtillot and Renne, 2003; Wignall, 2001, 2005; Bond and Wignall, 2014; Ernst, 2014; Courtillot and Fluteau, 2014; Courtillot et al., 2015; Bond and Grasby, 2017-this issue). This has become even more dramatically demonstrated with the improved U-Pb age constraints which increasingly now show a precise correlation between some LIP events and corresponding extinction boundary. The most compelling examples (and



Fig. 1 (continued).

those with the greatest precision in dating) are currently the Siberian Traps (252 Ma), CAMP (201 Ma), and the Deccan (ca. 66 Ma) LIPs (Figs. 1, 3), whose current dating matches precisely in age to the Permian–Triassic, Triassic–Jurassic, and Cretaceous–Tertiary, boundary extinctions, respectively (Blackburn et al., 2013; Burgess and Bowring, 2015; Schoene et al., 2015). These 'smoking gun' examples are summarized below.

2.1. Strongest correlations-'smoking guns'

New U-Pb dates on Siberian Traps LIP units (volcanic and intrusive rocks) demonstrate that much of the total lava/pyroclastic volume was erupted over <0.5 Myr, before and during the end-Permian mass extinction, and that magmatism continued for at least another 0.5 Myr after the extinction event (Burgess et al., 2014; Burgess and Bowring, 2015), building on previous U-Pb and Ar-Ar dating (e.g. Kamo et al., 1996; Reichow et al., 2009).

Similarly, high precision U-Pb dating on units of the 201 Ma CAMP event (Figs. 1, 3) demonstrate synchroneity between its earliest volcanism and the end-Triassic extinction, in multiple pulses over ~600 kyr, both at the extinction event and during the start of the subsequent biologic recovery (Blackburn et al., 2013; see also Schoene et al., 2010). These precise U-Pb data confirm the link with the Triassic-Jurassic extinction event previously proposed on the basis of earlier Ar-Ar dating, paleomagnetism, and also constraints from precession studies (Olsen et al., 2003; Marzoli et al., 1999, 2004; Knight et al., 2004; Verati et al., 2005; Nomade et al., 2007).

Finally, high precision U-Pb zircon geochronology on the Deccan shows that the main phase of eruptions initiated at 66 Ma, ~250 kyr before the Cretaceous-Paleogene boundary and that >1.1 Mkm³ (=×10⁶ km³) of basalt erupted in ~750 kyr (Schoene et al., 2015). These data as well as earlier less precise geochronology (40 K- 40 Ar Cassignol–Gillot technique, Ar-Ar, and based on paleomagnetic data (Chenet et al., 2007, 2008, 2009; Knight et al., 2003; Renne et al., 2015)) are consistent with the hypothesis that the Deccan LIP contributed to the end-Cretaceous environmental change and biologic turnover that culminated in the marine and terrestrial mass extinctions.

Of the five largest extinction events (Fig. 3) only the major Ordovician–Silurian boundary event has not been correlated with a LIP event, although recent research has identified potential candidates (Section 3.2.5.3). Supplementary Table 1 provides a summary of Phanerozoic LIP events and their confirmed and speculative links with biostratigraphic boundaries and associated extinctions, along with information on kill mechanisms where available.

Note that the present paper is not intended to imply that LIPs are the only driver of mass extinctions in the geological record. However, given their huge scale and typical short duration (<5 Myr), along with associated massive thermal, gas and fluid inputs into the environment, research is increasingly showing that LIPs can exert major global shifts in environmental conditions at the Earth's surface through geological time. This is particularly true for those short term (few Myr) shifts in environmental conditions. As noted above, the longer duration excursions are more likely linked to the plate tectonic cycle. In addition, an important driver of extinction events is bioevolutionary changes (e.g. Algeo et al., 2016). For instance, the development of vascular land plants can be linked to Middle and Late Devonian environmental effects including mass extinctions (Algeo and Scheckler, 1998; Algeo et al., 1995, 2001). Similarly, bioevolutionary changes associated with the Great Ordovician Biodiversification Event (GOBE) are associated with dramatic environmental changes including the end-Ordovician extinction (e.g. Algeo et al., 2016 and references therein). Before considering the specific role of LIPs it is necessary to consider the other type of large size, but short duration event that has been frequently proposed a driver of catastrophic environmental change, namely bolide impact.

2.2. Meteorite impacts versus LIPs

There has been a heated debate for more than three decades over whether global extinctions are caused by meteorite impacts and/or LIP events. Those supporting the impact connection cite the close correspondence in age between the large Chicxulub impact event and the end-Cretaceous extinction event (e.g. Alvarez et al., 1980; Hildebrand et al., 1991; Schulte et al., 2010; Richards et al., 2015). Other bolideextinction event correlations have been proposed (see Supplementary Table 1) but each candidate requires more precise dating. For instance, the ~50 km diameter Siljan impact (Sweden) broadly correlates with the Frasnian–Famennian extinction in the Devonian (Keller, 2005; Bond and Wignall, 2014; Bond and Grasby, 2017-this issue). The ~23 km-diameter Rochechouart impact structure of the French Massif Central yielded a 40 Ar/ 39 Ar dating of sanidine (201.4 \pm 2.4 Ma, that would correspond to about 203.4 Ma, recalculated after Renne et al. (2010) and adularia (200.5 \pm 2.2 Ma; 2 σ) (Schmieder et al., 2010; Youbi et al., 2014). The similarity with the Triassic-Jurassic U-Pb age of 201.36 \pm



Fig. 2. Global LIPs barcode record with selected labelling (updated from Ernst, 2014). Each LIP name is followed by location information: Am = Amazonia, AS = Asia, AU = Australia, CA = Central America, CC = Congo craton, EU = Europe, gLau = Greenland portion of Laurentia, Lau = Laurentia, Bal = eastern Baltica, SFC = Sao Francisco craton, Kal = Kalahari craton, Kap = Kaapvaal craton, KKC = Karelia-Kola craton, NA = North America, NAC = North Australian craton, NC = Nain craton, PA = Pacific, Pil = Pilbara craton, SA = South America, Sib = northern Siberian craton, Sla = Slave craton, Sup = Superior craton, WAC = West African craton, Wyo = Wyoming craton, Yil = Yilgarn craton, Zim = Zimbabwe craton. Names for Silicic LIPs are in red color, for continental LIPs are in black and for oceanic LIPs are in blue.

0.17 Ma (Schoene et al., 2010; Blackburn et al., 2013; Wotzlaw et al., 2014) needs to be tested by more precise U-Pb dating and chemostratigraphic and magnetostratigraphic studies. Another possible correlation is a significant group of L-chondrite meteorites impacting in the Middle Ordovician period, 467.3 ± 1.6 million years ago due to fragmentation of a parent body at this time and linked to the GOBE (Schmitz et al., 2007, 2016; for background on GOBE see Algeo et al., 2016).

Overall correlations between other impacts and other extinction events are less clear because of the uncertainty in the ages of most large impacts and await high precision U-Pb dating (e.g. Jourdan et al., 2009; Racki, 2012). The other long-standing source of uncertainty in the literature has been in the dating of stage boundaries that mark these biota changes (including extinction events), but this is becoming less of concern given steady progress in U-Pb dating of these boundaries (e.g., Schoene et al., 2015; Blackburn et al., 2013; Wotzlaw et al., 2014; Burgess and Bowring, 2015; Schoene et al., 2015; Gradstein et al., 2012a, 2012b; Ogg et al., 2016 and references therein).

Another consideration is a proposed link between impacts and LIP events. Petersen et al. (2016) note separate pulses in the extinction record that are linked to the Deccan LIP and the Chicxulub impact. It has been speculated (Richards et al., 2015; see also Renne et al., 2015) that the Deccan LIP was already in progress, and then the Chicxulub

impact generated seismic energy that triggered a transient increase in the effective permeability and thereby increased the rate of melt extraction from the plume head causing the voluminous Wai pulse of the main pulse of the Deccan LIP. Others have promoted (Jones et al., 2002) and discounted (e.g. Ivanov and Melosh, 2003) a direct link between major bolide impact and voluminous LIP scale magmatism at the site of impact or antipodally (see discussion in Ernst, 2014).

The present review focusses on the remarkable spectrum of known links between LIP events and extinction/environmental effects. If future work confirms a role for bolide impact in specific events (in addition to Chicxulub for the end-Cretaceous extinction) then the environmental effects of the bolide impact can be evaluated within the framework provided by the LIP record. In such cases the notion by White and Saunders (2005) of a "one-two punch" of a LIP and bolide impact would apply in cases where a temporal link between evidence of impact and extinction can be found.

3. Kill mechanisms

There are several 'key' mechanisms responsible for massive biological changes, which are discussed below and which can be partly linked to the LIP record: global warming, global cooling, anoxic events, ocean



Fig. 3. Correlation of LIP events with extinction events, updated from Ernst (2014). This figure shows the genus extinction intensity, i.e. the fraction of genera that are present in each interval of time but do not exist in the following interval. The data are from Rohde and Muller (2005), and are based on Sepkoski (2002). The curve is based on marine genera with the LIP record superimposed.

(Modified from Fig. A2 in Supplementary files of Rohde and Muller (2005) to include links with the LIP record.)



Fig. 4. Phanerozoic record of mass extinctions, temperature conditions (Hothouse (H), Greenhouse (G), Icehouse (I)), oceanic anoxic events, mercury/TOC anomalies, in comparison with the Phanerozoic LIP record. Incorporates environmental data presentation style after Percival et al., 2015). Open circles are carbon-isotope excursion and/or black shale not recognized as a OAE Information mainly from Supplementary Table 1. Global temperatures shifts between Hothouse, Greenhouse and Icehouse mostly after Kidder and Worsley, 2010). LIPs are marked by red bars, and their lower volume continuations, by pink bars.

acidification, introduction of toxic metals and gases, removal of bioessential elements, sea-level changes, and the stepwise oxygenation of the Earth's atmosphere (Figs. 4, 5, 6). Specific kill mechanisms apply to the atmosphere, to the ocean, and typically to both (given interchange between the atmosphere and ocean). Excellent reviews on aspects of the LIP-environmental link exist, such as Courtillot (1999), Wignall (2001, 2005), Bond and Wignall (2014), and Kidder and Worsley (2010, 2012), and Bond and Grasby (2017-this issue). However, the fast-evolving literature on both aspects (environmental changes and the LIP record) justify another review which explores not only the Phanerozoic linkages, but also considers the LIP record more comprehensively and expands the discussion into Precambrian time.

3.1. Global warming linked to greenhouse gases from LIPs

3.1.1. Global temperature changes and cycling of Earth between Greenhouse, Hothouse and Icehouse conditions as a controlling context

The Earth's environment goes through a range of average temperature conditions and transitions between these conditions (Greenhouse to Hothouse and Icehouse). This cycling between these basic conditions has become a framework for capturing the essential characteristics of the overall environmental conditions during the Phanerozoic. As described by Kidder and Worsley (2010, 2012) 70% of the time the Earth is in a Greenhouse condition. The transitions to Hothouse climates (grouped with Greenhouse climates in terminology of Wignall, 2005; see also Whiteside and Grice, 2016) are strongly correlated with LIP events (Fig. 4). The LIP link with ice ages is also robust and is discussed below, and is caused by sulphur aerosols, and/or from CO_2 drawdown due to weathering of emplaced lavas (Section 3.2). Kidder and Worsley (2010) note that a Hothouse climate reverts to a default Greenhouse state when the LIP activity ends.

3.1.2. Global warming

The geological record through stable isotopic proxies such as δ^{13} C shows that abrupt increases in the atmospheric concentration of greenhouse gases have occurred many times during the Phanerozoic (e.g. Petersen et al., 2016). The release of several thousand gigatons of isotopically light carbon gases has been proposed to be the cause of warm periods at a number of times in the Phanerozoic (e.g. Kidder and Worsley, 2010, 2012), each correlated with a LIP event (Supplementary Table 1; Figs. 4, 5). In particular, high precision geochronology shows a robust link between known LIP events and associated bursts of CO₂ that caused



Fig. 5. Flow chart showing environmental effects for both continental and oceanic LIP. Continental LIP modified after Bond and Wignall (2014). Oceanic LIPs modified after Kerr (2005, 2014). Delta notation used for isotopic ratios (e.g. δ0 for δ180)



Fig. 6. Link between LIPs and progressive oxygenation of the Earth. Oxygenation curve from Fig. 1 in Lyons et al. (2014). Distribution of Paleoproterozoic glacial intervals from Gumsley et al. (2017). Source of information on other glacial intervals from other references discussed in text. Global LIP barcode shown with specific events relevant to the glacial and oxygenation record labelled. End of LTE = end of Lomagundi-Jatuli Excursion. Paleoproterozoic glaciations (after Gumsley et al., 2017) are: R = Rietfontein, G-R = Gowganda-Rooihoogte, B-D = Bruce-Duitschland, RL-M = Ramsley Lake-Makganyene. Location labels (in parentheses) after LIP names explained in Fig. 2 caption. Note that the period roughly between 1.8 and 0.8 Ga has been referred to as the 'boring billion', reflecting the relative environmental stability during this period (Holland, 2006),

global warming at the Permian-Triassic boundary (252 million years ago; Siberian Traps LIP), Triassic-Jurassic boundary (ca. 201 Ma; CAMP LIP); the Toarcian stage of the Early Jurassic (ca. 183 Ma; Karoo-Ferrar LIP), and in the initial Eocene (ca. 55 Ma; second pulse of NAIP, North Atlantic Igneous Province LIP). The magnitude of the temperature increases estimated from the oxygen isotopic ratio $\delta^{18}\text{O}$ is 5 to 10 °C (e.g. Pearce et al., 2008). Petersen et al. (2016) noted that a 8 °C positive temperature excursion is associated with the Deccan LIP. Keller et al. (2016) noted a hyperthermal warming at the onset of the main phase of Deccan eruptions at the base of C29r and a major hyperthermal warming just preceding the end-Cretaceous mass extinction. Saunders (2016) argued for a 15 °C temperature increase due to the Siberian Traps LIP at the Permo-Triassic boundary and a temperature increase of 4-10 °C (depending on latitude) associated with the PETM, correlated with the second pulse of the NAIP. Brand et al. (2015) interpreted an >34 °C increase associated with the end Permian extinction linked to the positive feedback provided by release of voluminous gas hydrates (Section 3.1.4).

3.1.3. Importance of the intrusive component

Much of the literature has emphasized the gas release produced by the volcanic component of the LIP. However, with the discovery of hydrothermal vent complexes (HVCs) it was shown that gas release from the intrusive component of LIPs potentially has an equal or even greater climatic effect (Fig. 5). HVCs are an essential component of LIPs (Jamtveit et al., 2004; Planke et al., 2000; Svensen et al., 2006, 2007, 2009; Neumann et al., 2011; Frieling et al., 2016). They originate from explosive release of gases generated when thick sills (>50 m) are emplaced into volatile-rich but low permeability sedimentary strata. Up to 5–10 km across at the paleosurface, these vents connect to underlying dolerite sills at paleodepths of up to 8 km. They have been observed in association with the Siberian Traps, NAIP, Karoo, and others, and are predicted for other LIPs such as CAMP (e.g. Svensen et al., 2009).

In addition, it is recognized that major methane release can occur through emplacement of intrusions into sedimentary basins associated with new ocean opening (Berndt et al., 2016) lending further support to the hypothesis that rapid climate change can be triggered by magmatic intrusions into organic-rich sedimentary basins. Additional support for the importance of the intrusive component for the CAMP event is provided by Lindström et al. (2015a) (see also Hallam and Wignall, 2004; Wignall and Bond, 2008) who noted that seismites (earthquake-induced soft-sediment deformation) across Europe (Simms, 2007) were concentrated in strata near the end-Triassic mass extinction interval, which they attributed to emplacement of CAMP-related intrusions releasing gases.

The most detailed calculation of the climatic effect of such HVCs is based on those associated with the Siberian Traps LIP. The end-Permian crisis can be attributed to the effect of Siberian Traps sills on host evaporites (producing halocarbons) and organic-rich deposits (producing greenhouse gases CH_4 and CO_2), which are then transported to the surface via HVCs and into the atmosphere. Basin-scale gasproduction-potential estimates show that metamorphism of organic matter and petroleum by intrusions could have generated > 100,000 Gt of CO₂ (e.g. Svensen et al., 2009).

The host lithologies for the intrusive component of a LIP exerts significant controls on the environmental consequences of the LIP. Contact metamorphism around intrusions within dolomite, evaporite, coal, or organic-rich shale host rocks can generate large quantities of greenhouse and toxic gases (CO₂, CH₄, SO₂) (Ganino and Arndt, 2009, 2010). In some cases, such gases might not reach the surface through HVCs—if they are trapped by overlying rocks that are not permeable (Nabelek et al., 2015). The permeability of the overylying rocks is therefore a factor affecting LIP lethality from the intrusive component.

3.1.4. Gas release volume, composition, and altitude reached

With respect to gas release from LIP volcanism, three aspects are important: gas release volumes (both of the magmatic event as a whole and from individual volcanic eruptions), gas release composition, and gas release height (e.g. Self et al., 2014, 2015; Jones et al., 2016a). As noted below, positive feedbacks can magnify the environmental effects. For instance, additional warming can result from processes such as destabilization of gas hydrates and increased wildfire activity that release further CO₂ into the atmosphere.

3.1.4.1. Gas volume. One factor is the total volume of the LIP, with an expectation that larger LIPs will have a greater environmental effect, by releasing a correspondingly greater volume of volatiles. However, it has been noted by Wignall (2001) that the total volume of a LIP is an imperfect guide to magnitude of its extinction-inducing climatic effects. Most dramatically, the largest LIP event, the reconstructed ca. 70 Mkm³ ca. 120 Ma Ontong Java–Manihiki–Hikurangi oceanic plateau (Taylor, 2006), also termed Ontong Nui (Chandler et al., 2012) or Greater Ontong Java (e.g. Charbonnier and Föllmi, 2017; but see original use of this term by Ingle and Coffin, 2004, for Ontong Java and nearby ocean basin flood basalts) is not associated with an elevated level of extinctions, but is instead associated with a more modest environmental expression as an anoxia event, the Aptian-aged Selli Ocean Anoxia Event (OAE) (Tejada et al., 2009).

The absence of a strong relationship between LIP size and magnitude of extinction event underlines the complexity of their relationship. What is likely more important than the overall volume of the event is the duration of short-term pulses extending down to the scale of single volcanic flows. The results of Prave et al. (2016a) on geology and geochronology of the Eocene–Oligocene volcanism of the Tana Basin in Ethiopia reinforce the view that it is not the development of a LIP alone but its rate of effusion that contributes to inducing global-scale environmental change. As shown in Bryan et al. (2010), LIPs are associated with the largest volcanic events in Earth history including some areally extensive $(10^4–10^5 \text{ km}^2)$ basaltic lava flow fields and also silicic ignimbrites. The gases released are dominantly H₂O, followed in abundance by CO₂ and also SO₂ and halogens (e.g. Self et al., 2014, 2015).

3.1.4.2. Gas composition. As long realized, global warming is associated with an increase in greenhouse gases, such as CO_2 and CH_4 . In contrast, release of sulphur dioxide gas can lead to both greenhouse warming and then to global cooling (when it is converted to sulphuric acid and then to sulphate aerosols). Ozone-destroying halogens can also be released by volcanism, and also via the intrusive component of LIPs interacting with volatile rich sediments and being released to the atmosphere through hydrothermal vent complexes (HVCs) (Section 3.1.3). Mercury can be released into the atmosphere from volcanic events with deleterious effects (see Section 3.6.2).

Carbonatites are associated with many LIPs (e.g. Ernst and Bell, 2010), and Ray and Pande (1999) suggested that carbonatite-alkaline intrusions could contribute to an extinction event by releasing high amounts of CO_2 and SO_2 into the atmosphere in a very short time.

3.1.4.3. Gas release height. An important factor is the release altitude, since gases and particles that are released into the stratosphere as aerosols will have a greater and longer lasting effect on climate (1–3 years) than material reaching only the tropospheric level (1–3 weeks). (Robock, 2000; Wignall, 2001; Robock and Oppenheimer, 2003; see also Self et al., 2005, 2006, Bond and Grasby, 2017-this issue). Supereruptions are particularly important in carrying gases to the troposphere (e.g. Self and Blake, 2008; Stern et al., 2008). See Section 3.2.1 for additional discussion.

3.1.4.4. Destabilization of gas hydrates. The increases in Earth's temperature due to greenhouse gases, can destabilize methane hydrate (clathrate) mega-reservoirs causing massive release of the greenhouse gas methane into oceans and the atmosphere, representing a strong positive feedback (e.g. Wignall, 2001; Jahren, 2002; Dickens, 2011) and creating a short-duration negative δ^{13} C spike (e.g. 200 kyr) (Pálfy et al., 2001; Retallack, 2001; Beerling and Berner, 2002; Schoene et al., 2010; Berndt et al., 2016). The effect of methane release can be catastrophic. As suggested by Brand et al. (2015), the end-Permian extinction involved a global warming of 8 to 11 °C due to isotopically light carbon dioxide from the Siberian Traps LIP, which then triggered the sudden release of methane from permafrost and shelf sediment hydrate leading to a catastrophic global warming of >34 °C.

3.1.4.5. Increased wildfire activity. The increase in global temperature can be associated with an increase in wildfire frequency and intensity. For instance, charcoal records from Greenland, Denmark, Sweden and Poland show increased wildfire activity (leading to further CO_2 release) in association with the CAMP event (Lindström et al., 2015b). A related effect is noted by Grasby et al. (2011) who suggested that deposition of coal fly-ash generated by magma-coal pyrometamorphism in the Siberian Trip LIP resulted in toxic marine conditions. This suggests that increased ash deposition from wildfires would be similarly deleterious.

3.1.4.6. Additional indirect effects. There are also indirect effects such as the interaction of a CO_2 rich atmosphere with ocean to produce anoxia (e.g. Percival et al., 2015) and together with H₂S to produce acid rain and ocean acidification (Section 3.5). On the other hand, the timing of increased CO_2 is also correlated with timing of increased silicate weathering (see below), which provides a break on runaway greenhouse conditions by fostering cooling (Section 3.2; Kump et al., 2000; Goddéris et al., 2014; McKenzie et al., 2016).

3.2. Global cooling

Earth also goes through periods of global cooling (Fig. 4, Supplementary Table 1) that can include global, near global or regional glaciations which are observed in the Archean, Paleoproterozoic, Neoproterozoic, Ordovician, Permo-Carboniferous Eocene-Oligocene, Eocene to middle Miocene and Quaternary times (e.g. Evans et al., 1997; Augustin and EPICA Community Members, 2004; Eyles, 2008; Stern et al., 2008; Hoffman, 2009; Cather et al., 2009; Bradley, 2011; Prave et al., 2016a). There is an extensive literature on global and regional glaciations and a variety of causes have been considered (e.g. Raymo, 1991; Berner, 2004 and references therein). For instance, glaciations have been linked to silicate weathering during major orogenic episodes such as the formation of the Himalayas (Cenozoic glaciation) and the assembly of Pangea (Permo-Carboniferous glaciation). Major land plant innovations have also been thought to be a significant factor in causing or at least contributing to glaciations, e.g. for the Ordovician glaciation (Lenton et al., 2012; Kidder and Worsley, 2010; Algeo et al., 2016). It is also now recognized that LIPs can contribute to global cooling via at least two different mechanisms: due to LIP input of SO₂ into the atmosphere (and conversion to sulphate aerosols) and to the weathering of LIP units, especially basalts.

3.2.1. Volcanic Winter

One mechanism for cooling the climate relates to the amount of SO_2 which is a greenhouse gas and causes warming for days to weeks. But on a longer term it causes cooling because it forms sunlight blocking sulphate aerosols (e.g. Bond and Wignall, 2014). The role of sulphur degassing as a kill mechanism is suggested by Callegaro et al. (2014) who showed that the continental LIPs such as the CAMP and Deccan (strongly linked to extinction events) have basalts with high sulphur content, up to 1900 ppm while the less damaging (not associated with mass extinction) Parana-Etendeka LIP has basalts with much lower magmatic sulphur content (<800 ppm).

The timing can be complicated with initial cooling associated with sulphate aerosols, following by warming as greenhouse gases build up and then further cooling can occur if significant erosion of the flood basalts then occurs, drawing down CO_2 , or generation of sulphate aerosols during active LIP phases might simply act to reduce the net warming. The situation might be different with SLIPs, which tend to emit much lower levels of greenhouse gases than LIPs, and so the cooling effect may be more effective for SLIPs (D. Kidder, Pers. Comm., 2016).

The effects can be even more dramatic if the gases are injected into the stratosphere via Plinian eruptions. So called "super-eruptions" (Self and Blake, 2008), can cause climatic cooling on a global scale (Robock, 2004; Self, 2006; Self and Blake, 2008). This linkage led to development of the "Volcanic Winter" concept of Rampino et al. (1988), which focusses on short-term (1-3 years) climate cooling caused by explosive volcanism. Explosive volcanism mainly affects climate by injecting sulphur dioxide (SO₂) into the stratosphere. Volcanic ash is also injected but this settles quickly out of the atmosphere and so causes little cooling; in contrast, sulphur aerosols can remain suspended for a year or more. The geographic extent of cooling resulting from volcanic aerosols depends on eruption latitude and stratospheric winds, with equatorial eruptions having the greatest effect (Self, 2006). Stern et al. (2008) developed the hypothesis that explosive volcanism was at least partly responsible for Neoproterozoic climate change, synopsized as the "Volcanic Winter to Snowball Earth" (VW2SE) hypothesis.

3.2.2. Weathering and CO₂ drawdown

The other dramatic mechanism for driving cooling on the Earth's surface is related to silicate weathering. On the broadest scale, the extent of supercontinent assembly is linked to broad peaks and valleys in atmospheric CO₂ abundance lasting 10s of Myr (Goddéris et al., 2014). However, some dramatic changes in the CO₂ level, particularly those that are of short duration (e.g. on the scale of a few million years) can be linked to the weathering of LIPs. Goddéris et al. (2003) discuss the following sequence of events: at the beginning of the LIP event, atmospheric CO₂ first rises due to degassing of hot basaltic lavas. Immediate global warming is rapidly counteracted by the increasing consumption of atmospheric CO₂ due to continental silicate weathering (including the weathering of flood-basalt material). Note that weathering of continental silicates is enhanced under a warmer and (assumed) wetter climate (at lower latitudes), and basaltic volcanic rocks weather about five to ten times faster than granitic rocks (Dessert et al., 2003). Chemical weathering rates double when temperature goes up by 10 °C (Ruddiman, 2008; see also Walker et al., 1981).

 CO_2 drawdown due to weathering of LIPs leads to idea that erosion of flood basalts can initiate global cool down and even glaciations. Based on weathering laws for basaltic lithologies (Dessert et al., 2003) and on climatic model results, weathering of a 6 Mkm² basaltic province located within the equatorial region (where weathering and consumption of CO_2 are optimal) could be sufficient to trigger a snowball glaciation (Goddéris et al., 2003). Note that the cooling effect introduced by chemical weathering of new LIP basalts might be amplified during warm-climate intervals, not only by the fact that the climate is warmer, but also by the expansion of warm climates to higher paleolatitudes. This would mean that LIP basalts that erupted at mid-latitudes might have a much greater contribution to cooling the climate than they would during an Icehouse climate. Furthermore, the poles tend to moisten considerably at such times, so their weathering potential might increase too, at least in summer (D. Kidder, Pers. Comm., 2016). For instance, there was an abrupt increase in chemical weathering in the Early Triassic potentially linked with the Siberian Traps LIP which was at mid-high latitudes at this time (Sheldon, 2006; Algeo and Twitchett, 2010). So polar regions which warm in Greenhouse times (with summer temperatures of around 15 °C) and more so in Hothouse times can become moist and potentially have enhanced weathering (Kidder and Worsley, 2004, 2010; Taylor and Ryberg, 2007, the latter noting tree growth at polar latitudes).

The sedimentary record should reflect certain trace element and isotopic abundances if LIPs are being massively weathered in contrast to average continental crust. For example, erosion of LIPs (and particularly their flood basalts) should produce geochemical/isotopic characteristics which are typical of a dominantly mafic provenance, for example through the input of radiogenic Nd, and unradiogenic Sr and Os (e.g. Mills et al., 2014; Cox et al., 2016). An example is the mafic Nd and Sr isotopic shifts in sediments associated with the timing of Neoproterozoic LIP events (e.g. Cox et al., 2016).

3.2.3. CO₂ drawdown due to silicic magmatism

The effect of silicic LIPs on cooling can be dramatic. Cather et al. (2009) demonstrated that during middle Eocene to middle Miocene time, the development of the Cenozoic Icehouse was coincident with a prolonged episode of explosive silicic volcanism, the ignimbrite flareup of southwestern North America. They present geochronologic and biogeochemical data suggesting that, prior to the establishment of full glacial conditions with attendant increased eolian dust emission and oceanic upwelling, iron fertilization by great volumes of silicic volcanic ash was an effective climatic forcing mechanism that helped to establish the Cenozoic Icehouse. They further conclude that most Phanerozoic cool-climate episodes were coeval with major explosive volcanism in silicic LIPs, suggesting a common link between these phenomena, which they term the Icehouse-SLIP hypothesis (Cather et al., 2009).

3.2.4. End of ice ages

Global weathering leads to ice age and albedo increase because of snow/ice cover which reflects more energy back into space. This means that volcanism might be key to taking the planet out of a global ice age. However, a background low volcanic flux can also build up CO₂ to a tipping point, and so a LIP event is not required to end an ice age. As shown below the record is mixed on this point. The ca. 650-630 Ma end of the Sturtian glaciation and transition to the Marinoan glaciation is not associated with any LIP; the timing is linked with a peak time of subduction related magmatism in the Arabian-Nubian shield and east African orogen (Stern et al., 2008). However, the termination of two Paleoproterozoic glaciations are linked with LIPs (for more details see Section 3.2.5.1). The 2426 \pm 3 Ma Ongeluk LIP occurs at the end of the correlated Ramsey Lake (Huronian Basin) and Makganyene (Transvaal Basin) glaciations and is considered to be the cause of the end of the glaciation (Gumsley et al., 2017). Similarly, the 2250–2240 Ma Hekpoort LIP (Kaapvaal craton) and 2215–2210 Ma Nipissing-Ungava LIP (Superior craton) approximately mark the end of the Rietfontein glaciation (Gumsley et al., 2017).

3.2.5. LIPs and glaciations

In this section the history of glaciations in the Proterozoic and Phanerozoic is compared with the LIP record, and both temporal correlations and non-correlations are noted.

3.2.5.1. Paleoproterozoic glaciations. Three pulses of glaciation observed in the Huronian basin (H) on the southern edge of the Superior craton (e.g. Fig. 6; Young, 2013; Melezhik et al., 2013) can now be correlated with glaciations in the Transvaal basin (T) of Kaapvaal craton (Gumsley et al., 2017): Ramsey Lake (H)–Makganyene (T), Bruce

(H)—Duitschland (T) and Gowganda (H)—Rooihoogte (T) as well as a the younger Rietfontein (T). Two of these glaciations end with LIP events. The Ramsey Lake-Makganyene is followed by the 2426 \pm 3 Ma Ongeluk LIP, and the Rietfontein glaciation is followed by the ca. 2250–2240 Ma Hekpoort and 2215 Ungava-Nipissing LIPs. There can also be a link with the start of a glaciation. The oldest glaciation (Ramsey Lake-Makganyene) is preceded by (and perhaps influenced by) various 2.5–2.45 Ga units globally (Melezhik et al., 2013; Gumsley et al., 2017): the 2.51 Mistassini and 2.48–2.45 Ga Matachewan LIPs of the Superior craton, and in adjacent parts of Karelia-Kola (Ernst and Bleeker, 2010), and also the Woongara-Weeli Wolli LIP of the Pilbara craton (Ernst, 2014).

3.2.5.2. Neoproterozoic glaciations. The Neoproterozoic is another important time for global glaciations, Sturtian, Marinoan and Gaskiers which can be compared with the LIP record (Fig. 6). The Sturtian glaciation (ca. 717-660 Ma) is immediately preceded by the 725-715 Ma Franklin LIP of northern Canada (Macdonald et al., 2010) and coeval Irkutsk LIP in formerly attached southern Siberia (Fig. 6; Ernst and Bleeker, 2010; Ernst et al., 2016a). Cox et al. (2016) suggested a link based on the rapid CO₂ drawdown which they linked to both increased erosion in a tropical latitude and increased contribution of P to the oceans increasing biologic productivity and thereby further increasing weathering drawdown. There is no ca. 650-635 Ma LIP event currently recognized between the end of the Sturtian glaciation (at 660 Ma) or associated with the Marinoan glaciation (ca. 640-635 Ma). The ca. 580 Ma Gaskiers glaciation is similar to a number of LIP events that belong to a ca. 590-570 Ma pulse of the 615-555 Ma multi-pulsed Central Iapetus Magmatic Province (CIMP) (e.g. Ernst and Bleeker, 2010). This pulse includes the Grenville dykes of eastern Laurentia (at ca. 590 Ma), the Volyn flood basalts of Baltica at ca. 570 Ma (Shumlyanskyy et al., 2016a), and the ca. 580 Ma Ouarzazate intraplate magmatism of West Africa (Youbi et al., 2016; Ikenne et al., 2016).

3.2.5.3. Phanerozoic glaciations. The Hirnantian glaciation (ca. 440 Ma) can be broadly associated with postulated LIP magmatism that includes the ca. 440 Ma Suordakh dolerite event in eastern Siberia (Khudoley et al., 2013), the Ongnyeobong Formation volcanics in South Korea (Cho et al., 2014), flood basalts of Sierra del Tigre in Argentina (Retallack, 2015) and other magmatic units elsewhere (Millward and Evans, 2003; Millward, 2004; Buggisch et al., 2010; Huff et al., 2010; Kravchinsky, 2012; Perrier et al., 2012; Retallack, 2015). However, the scale and precise dating of these intraplate events are not currently well constrained. Permo-Carboniferous glaciations (300 to 260 Ma) are broadly linked with the widespread intraplate magmatism of the European North West African Magmatic Province (EUNWA or EUNWAMP, and its initiation as the 300 Ma Skagerrak LIP, and also the 260 Ma Emeishan LIP.

3.2.5.4. Complexities in the relationships. As shown above there are LIPs linked with the onset of glaciation, such as the 720 Ma Franklin-Irkutsk LIP with the start of the Sturtian glaciation and the ca. 580 Ma pulse of CIMP associated with the Gaskiers, and perhaps the 2.5–2.45 Ga LIPs associated with the Ramsey Lake-Makganyene glaciation. In such cases, either of the above-mentioned cooling mechanisms (sulphate aerosols and weathering of basalts) could be responsible for the cooling. In addition, there are examples of LIPs associated with the end of glaciations, such as younger phases of the ca. 580 Ma CIMP pulse with the Gaskiers glaciation and the 2426 Ma Ongeluk LIP with the Ramsey Lake-Makganyene glaciation and the ca. 2250–2240 Ma Hekpoort and 2215 Ungava-Nipissing LIPs with the end of the Rietfontein glaciation, in these cases representing global warming events that helped end these glaciations.

However, some LIPs that experienced extensive weathering did not result in global cooling. For instance, as demonstrated by Schaller et al. (2012) weathering of CAMP reduced atmospheric carbon dioxide significantly, but not to the point of stimulating glaciation. Also, some of the glaciations did not begin with a LIP. It has been observed that there is enhanced LIP activity at times of Precambrian supercontinent breakup (Ernst and Bleeker, 2010), and while there is a glaciation link with both the breakup of the Archean supercontinent (in the early Proterozoic; Section 3.2.5.1) and the breakup of Rodinia (ca. 725 Ma; Section 3.2.5.1), there is no glaciation associated with breakup of Nuna-Colombia (ca. 1400–1200 Ma).

Interestingly the Permo-Carboniferous glaciations are associated with a time of supercontinent assembly and presumably linked to enhanced silicate weathering during orogenesis. With these complexities, it can be inferred that there are important controls on global cooling besides LIPs, such as weathering of orogens and bioevolutionary changes such as increased C_{org} burial by land plants (as discussed above). Further research is necessary to properly assess the role of LIPs in some glacial events.

3.3. Oceanic anoxia events

3.3.1. Characteristics

Periods of oceanic environmental crisis are identified by black shales that are indicative of low, or oxygen-absent, deep-ocean conditions termed Oceanic Anoxia Events (OAEs) (e.g. Kerr, 1998, 2005; Meyer and Kump, 2008; Jenkyns, 2010; Du Vivier et al., 2014; Brazier et al., 2015; Percival et al., 2015, 2016; Chi Fru et al., 2016). A wide variety of causes have been attributed to the formation of OAEs such as enhanced preservation under restricted and poorly oxygenated conditions, or increased organic productivity in the oceans using up available oxygen. Kerr (1998, 2005) has emphasized the role of oceanic LIPs in causing such anoxia events, but as shown in Supplementary Table 1 and discussed below, some continental LIPs are also associated with and contributed to anoxic events.

3.3.2. Link with LIPs

Black shales indicative of global OAEs occur throughout the Phanerozoic (Jenkyns, 2010) and each of the major ones can be temporally linked to a LIP (Supplementary Table 1; see also Pearce et al., 2008; Percival et al., 2016). The Cretaceous was marked by a number of global OAEs, black-shale deposition, and $\delta^{13}C$ excursions correlated with oceanic-plateau formation, particularly around the Cenomanian-Turonian boundary (93.5 Ma) and during the Aptian (124–112 Ma) (Fig. 1). In addition, as noted by Kerr (2005), important Kimmeridgian to Tithonian (155–146 Ma) oil source rocks correlate with the formation of the Sorachi plateau in the western Pacific (Kimura et al., 1994) and would also be similar in age with the poorly-dated Shatsky-Tamu LIP (Sager et al., 2013; Heydolph et al., 2014; Ernst, 2014). Furthermore, the formation of Toarcian (187-178 Ma) black shales corresponds with the eruption of the Karoo-Ferrar LIP. The link between black shales and LIPs has become important in the context that black shales are a key source rock for hydrocarbons (e.g. Kerr, 2005; Ernst, 2014).

Those anoxic events with significant hydrogen sulphide are termed euxinic, and occur in the end-Permian, Late Devonian, and Cenomanian–Turonian extinctions (e.g. Kump et al., 2005) which are associated with the ca. 370 Ma Yakutsk-Vilyui and Kola Dnieper, 252 Ma Siberian Traps LIP, and ca. 90 Ma Caribbean-Colombian, HALIP, and Madagascar LIPs, respectively (see Supplementary Table 1).

3.3.3. Details of the Bonarelli (OAE2) event

There are times when multiple independent LIPs are occurring at the same time (Ernst and Buchan, 2002). One such time is at ca. 90–95 Ma, featuring the Madagascar, Caribbean-Colombian, High Arctic LIP (HALIP (younger pulse), which is also correlated with the short duration OAE2 event. Within this short duration event (0.71 ± 0.17 Myr at 94 Ma (Eldrett et al., 2015) there are signatures which can potentially identify the superimposed or sequential influence of these different LIPs. Eldrett et al. (2014) note the presence of trace metals (Cr, Sc, Cu and Co)

suggesting the influence of a LIP, that they suspect to be HALIP and which occurs in the middle of the anoxic event, and is therefore not the initial cause of this OAE2 event. However, the osmium isotope excursion by Turgeon and Creaser (2008) corresponds to the onset of the anoxic event and has been linked with the Caribbean Colombian LIP. In addition, a lead isotope study has linked OAE2 to the Caribbean-Colombian and Madagascar LIPs (Kuroda et al., 2007).

3.3.4. Anoxia events in the Precambrian

The temporal link between LIPs and global anoxia events is best characterized in the Phanerozoic, but the robustness of that link indicates that the Proterozoic and even late Archean black shale record should similarly be linked to LIPs (and in particular, to oceanic plateaus), but this prediction remains to be systematically examined. As noted by Kerr (2005) there seems to be a temporal association, throughout a significant proportion of geological history, between periods of global oceanic environmental crises, black-shale formation, and oceanic-plateau formation (Kerr, 2005). Unfortunately, in the Precambrian the oceanic plateau record is poorly preserved (Dilek and Ernst, 2008). Condie et al. (2001) suggested that there was a maxima in black shale abundance at 2.0-1.7 Ga, and also less significant peaks in the Late Neoproterozoic (800–600 Ma) and in the Late Archean (2.7–2.5 Ga). Each of these timings broadly correlates with times of enhanced LIP activity (Ernst, 2014). However, to be confident about a specific genetic link requires more precise dating for both the black shale events and the provisionally-correlated LIP events. One clear Precambrian correlation is between ca. 1880 Ma black shales (e.g. Bekker et al., 2010, 2014) with coeval LIPs such as the Circum-Superior LIP (Fig. 1) and others globally of similar age (e.g. Minifie et al., 2013; Ernst, 2014).

3.4. Ocean acidification—calcification crisis

High CO₂ and SO₂ in the atmosphere can lead to acid rain in the form of carbonic acid and sulphuric acid, and these gases can also transfer to the oceans and cause oceanic acidification with a loss of calcified marine biota (e.g. Kerr, 2005; Kiessling and Simpson, 2011; Hönisch et al., 2012). As shown by modeling, volcanic sulphur and CO_2 released by the Siberian Traps LIP caused widespread acid rain that directly contributed to the end-Permian mass extinction (Black et al., 2013); this same model also emphasized the importance of halogens and global ozone depletion). Clarkson et al. (2015) considers the ocean acidification associated with the end Permian extinction which is linked with the Siberian Traps LIP. Similarly, the fossil record at the end of the Triassic showing major loss of calcifying organisms is evidence for ocean acidification, linked to the CAMP event (Lindström et al., 2015b). The ocean acidification at the Cretaceous-Tertiary boundary linked to the Deccan LIP has been also documented in Punekar et al. (2014, 2016) and Font et al. (2014).

3.5. Sea level changes

There are major sea level changes (Haq and Schutter, 2008; Haq et al., 1987; Haq, 2014) and separating LIP induced sea level changes from those occurring due to broader climate changes remains a challenge. The controls on sea level changes are complex and occur over a range of time scales (e.g. Miller et al., 2005; Hannisdal and Peters, 2011; Ernst, 2014) with the broadest changes linked to the cycle of ocean opening and closing, and the short term third order excursions being more specifically linkable with LIPs. Such more rapid changes in sea level have a greater effect on the environment and its biota.

The arrival of a mantle plume (causing a LIP) beneath oceanic lithosphere should result in a rise in eustatic sea level because of isostatic uplift and displacement of water by the oceanic LIP itself and thermal expansion of seawater (e.g. Kerr, 1998, 2014; Lithgow-Bertelloni and Silver, 1998; Condie et al., 2001; Miller et al., 2005). Emplacement of oceanic plateaus produces moderately rapid sea-level rises (60 m/Ma), but then sea level slowly falls as a result of the decay of the thermal mantle anomaly (10 m/Ma) (Miller et al., 2005). On the other hand, a continental LIP will contribute to local relative sea level fall owing to regional (up to about 2000 km across) domal uplift above the plume, but if the LIP is associated with subsequent continental rifting and breakup then the formation of extensive new buoyant oceanic crust and lithosphere causes widespread flooding (and sedimentation) of shallow platform environments. Iron formations can also be linked, wherein oceanic LIP magmatism provides the dissolved iron that precipitates in these new shallow platform environments (Section 3.8.3; Isley and Abbott, 1999; Abbott and Isley, 2001; Bekker et al., 2010, 2014; Ernst and Jowitt, 2013).

Modeling of uplift associated with continental LIPs (e.g. Campbell, 2005) indicates that changes in topography of a km or more can occur over a few million years and extend over a scale of up to 1000 km radius about the plume centre (and cause local regression). Oceanic LIPs can have a topographic uplift as well as build-up of an volcanic construct, but are mostly subaqueous, and therefore their topographic effect will be expressed in global sea level rise, but on a short duration time scale of a few million years. Emplacement of the Ontong Java oceanic plateau would have caused an estimated sea-level rise of at least 10 m based on a calculation assuming Airy isostasy (Schubert and Sandwell, 1989; Coffin and Eldholm, 1994). A similar calculation also incorporating the nearby ocean basin basalts and formerly connected Manihiki and Hikurangi plateaus would yield at least 15 m of sea level rise. A wide region of western Europe was affected by rapid sea-level fall and subsequent rise associated with the Triassic-Jurassic boundary (Hesselbo et al., 2004), and therefore should be linked to the CAMP LIP (regression due to uplift?) and the associated opening of the central Atlantic Ocean (transgression?).

An additional minor factor is the effect of global warming on increasing seawater volume (Kerr, 2014). A rough order of magnitude of that effect is given as follows: Given a volumetric temperature coefficient of 0.000088 (1/°C) for water at 10 °C), http://www. engineeringtoolbox.com/volumetric-temperature-expansion-d_315. html using 0.000088 (1/°C) and a temperature change from 10° to 15 °C yields a volume increase of 0.044%. Given the area of world's oceans = 360 Mkm^2 , and volume of world's oceans = 1400 Mkm^3 then the average water depth increase associated with this 5° average temperature increase is = 0.044% * (1400,000,000/360,000,000) = 0.04% * 3.888 km = 1.7 m. A similar calculation using 0.000207 (1/°C) for 20 °C and a temperature change of 20 °C to 25 °C yields a water depth increase of 4 m. On the other hand, cooling (potentially linked to LIPs; Section 3.2.4) and increased storage of water in polar ice can yield dramatic sea level drops. For instance, a sea level drop of nearly 100 m was associated with the Hirnantian extinction and associated glaciation (Harper et al., 2014; Brenchley et al., 2006).

3.6. Effect of toxic metals

3.6.1. Mercury

Toxic metals such as Hg, Os, Fe, Mo, Pb, Mn and As released by LIP events can represent a direct kill mechanism (e.g. Sanei et al., 2012; Vandenbroucke et al., 2015; Percival et al., 2016). Mercury is a particularly significant toxic metal, in part because it is produced by volcanism and in its metal state it is a volatile and so can be globally distributed with a residence time of approximately 1–2 years before oxidizing and binding to clays and organics (e.g. Font et al., 2016). Thus, volcanic activity may be recorded as enrichments in sedimentary mercury (measured as Hg/TOC) (Sanei et al., 2012, and references therein). Elevated mercury levels have been recognized in association with a least five LIP events (Fig. 4) including the Siberian Traps (e.g. Sanei et al., 2015; Thibodeau et al., 2016), Karoo-Ferrar (Toarcian) (Percival et al., 2015), and Deccan (Adatte et al., 2015; Keller et al., 2015; Adatte et al., 2016; Font et al., 2016). The mercury record for the PETM associated with NAIP LIP is

discussed by Khozyem et al. (2016). Jones et al. (2016c) revealed several major mercury peaks that indicate LIP volcanic contributions both before, at and after the Ordovician mass extinction, even though no LIP is known to date (but is speculated upon, Section 3.2.5.3). All these observations of LIPs as a source of environmental mercury are also consistent with mercury deposits spatially and age-wise correlated with the Siberian and Tarim LIP events (Borisenko et al., 2006). Most recently a mercury anomaly is matched with the timing of the largest LIP, Ontong Java oceanic plateau and reconstructed portions (Charbonnier and Föllmi, 2017).

3.6.2. Teratological (malformed) assemblages of fossil plankton

Metal toxicity represents an important contributor to environmental crises that can represent a kill mechanism associated with extinction events. One proxy for monitoring the effects is teratological (malformed) assemblages of fossil plankton (Munnecke et al., 2012; Vandenbroucke et al., 2015) or aberrant, i.e. abnormal, and thus probably non-viable pollen and spores (Lindström et al., 2015b). These authors suggest that the malformed effect is a harbinger of extinction events that these are an initial response to metal toxicity, and is specifically linked to the CAMP event. However, abnormal fossil morphologies can be found in most fossil assemblages at any given time and they tend to increase with increasing environmental stress that may or may not be associated with metal toxicity (Keller, Pers. Comm. 2016). In the study of Vandenbroucke et al. (2015), the two events discussed, the end-Ordovician Hirnantian event and the late Silurian (Pridoli) event are not associated with a known LIP (but see discussion in Section 2.1). Interestingly, the metal enrichment (Fe, Mo, Pb, Mn, and As) associated with the late Silurian (Pridoli) extinction event (Vandenbroucke et al., 2015) are not metals that are normally preferentially enriched in LIPs, but are metals associated with sulphide mineralization.

3.7. Depletion in bio-essential elements and nutrients

Another proposed kill mechanism is the depletion of bioessential elements such as Se, Mo, Ce, Cd, Tl, and P which can affect bioproductivity, carbon burial and oxygen release (Large et al., 2015). In particular, severe depletions in selenium and such trace elements at the end-Ordovician, end-Devonian and end-Triassic periods, correlate with those mass extinctions. The end-Triassic is correlated with the CAMP LIP event, the end-Devonian with a pulse of the Kola-Dnieper, and/or Yakutsk-Vilyui LIPs (Figs. 1, 2), and as mentioned above, the end-Ordovician extinction has indications of mafic magmatism involvement. Long et al. (2016) also suggest decrease in such bio-essential trace elements during global anoxia events, which as indicated above (Section 3.3) can be linked to LIPs. Grasby et al. (2016b) inferred a "nutrient gap" for the Siberian Traps LIP associated with the Permian-Triassic extinction as monitored by nitrogen stable isotopes.

3.8. Oxygenation of the atmosphere and ocean

Another important dramatic environmental change in Earth history is the oxygenation of the atmosphere. Geochemical and isotopic data suggest that oxygenation of the Earth's atmosphere occurred in two broad steps (Fig. 6), in the Paleoproterozoic, affecting the shallow ocean and in the Neoproterozoic, also affecting the deep ocean, and is linked with major glaciations (e.g. Frei et al., 2009; Lyons et al., 2014; Gumsley et al., 2017; see Section 3.2.4 for the link of LIPs and glaciations).

3.8.1. Great oxygenation event

Previous studies have constrained the Paleoproterozoic Great Oxidation Event (GOE) to between 2.45 and 2.2 Ga. The paper by Luo et al. (2016) identify this transition in a continuous sedimentary sequence in the Transvaal Supergroup, South Africa where the sulphur isotopic signal in diagenetic pyrite changes from mass-independent to becoming mass-dependent. These data date the GOE to 2.33 Ga and suggest that oxygenation occurred rapidly, over 1 to 10 Myr. A plausible mechanism for linking LIPs and oxygenation is that the LIP event leads to a burst of biological productivity that releases oxygen to the atmosphere. The timing of this specific transition does not match with any known major LIP, but does overlap with the newly recognized ca. 2.33–2.31 Ga Kuito-Taivalkovski intraplate event in Karelia, which has unknown overall extent (Ernst, 2014; Salminen et al., 2014; Stepanova et al., 2015). A link with the older 2.5–2.45 Ga LIPs is also possible (Gumsley et al., 2017; Ciborowski and Kerr, 2016 see Section 3.2.5.1).

The period of oxygenation continued until the end of the Lomagundi carbon isotope excursion at ~2060 Ma (Ma) (Fig. 6). The termination of the GOE would be then linked with 2.06 Ga LIPs (Bushveld LIP of the Kaapvaal craton and the Kevitsa-Kuetsjärvi-Umba LIP of Karelia (Ernst, 2014).

A different angle for assessing the link between LIPs and the GOE is proposed in the study by Konhauser et al. (2009) which discusses the Paleoproterozoic oxidation event(s) and specifically the GOE as resulting from a "methanogen famine" caused by a depletion of oceanic nickel, which is essential for methanogens. This decrease in nickel availability is linked to a dramatic drop in the frequency of komatiite-bearing LIPs after ca. 2.7 Ga (associated with Archean-Proterozoic transition). This decrease in komatiites and their Ni supply to sea-water would lead to a die-off of methanogens (which produce methane). However, the apparent briefness of the GOE event at ca. 2.33 Ga is less consistent with such a broad mechanism occurring several hundred Myr earlier.

3.8.2. Neoproterozoic oxidation event—role of phosphorous enrichment by LIPs

Low-latitude weathering of Neoproterozoic LIPs (such as the 720 Ma Franklin and Irkutsk LIPs; Ernst et al., 2016a) which have substantial P content (740 ppm), resulting in a high flux of bioavailable P ($1-5 \times 10^9$ mol/yr may have been sustained for millions of years) to the ocean which increased primary productivity (Horton, 2015). This would trigger oxidation of the ocean-atmosphere system and thus contribute to the Neoproterozoic oxidation event (Horton, 2015; Cox et al., 2016). Additional Neoproterozoic oxygenation may also have occurred after the 720 Ma pulse. For instance, Canfield et al. (2007) suggested that a significant amount of the deep ocean oxygenation took place in association with the Gaskiers glaciation at about 580 Ma (which can be linked with LIPs (Section 3.2.2)).

3.8.3. Link with iron formations

Iron formations can reflect both oxygenation pulses (leading to Fe reduction and precipitation) but also Fe availability (due to LIPs) and favourable shelf settings for deposition (e.g. Bekker et al., 2010, 2014 and references therein) and the latter is generally more important. Specifically, there is a strong correlation between the timing of iron formations with LIPs (e.g. Isley and Abbott, 1999). It is inferred that LIPs produce Fe- and Si-rich hydrothermal plumes that rise and spread and precipitate on clastic-starved shelf settings. Such shelf settings are more common during breakup events (which are also linked with LIPs). As noted above oxygenation occurred in the late Paleoproterozoic and in the Neoproterozoic. As proxied by Cr isotopes, transient rise in oxygen contributed to the burst of banded iron formations 2.7–2.45 Ga which was prior to the GOE. However, there is also a LIP link in the Paleoproterozoic. For instance, the ca. 2426 Ma Ongeluk Formation is overlain by banded iron and manganese deposits of the Hotazel Formation (Gumsley et al., 2017).

However, the widespread iron formation at 1880 Ma was associated with a drop in oxygen as indicated by Cr isotopes (Frei et al., 2009). This apparent conundrum of an iron formation during decreased oxygen is resolved through recognition of widespread mafic-ultramafic magmatic (LIP) events throughout the world at this time (e.g. Minifie et al., 2013; Ernst, 2014) and their effect on seawater composition (Rasmussen et al., 2015). Specifically, enhanced submarine volcanism released large volumes of ferrous iron that overwhelmed prevailing oceanic sulphur and oxygen conditions, and was precipitated in shelf settings. Furthermore, Rasmussen et al. (2015) note that the end of this period of intense iron formation also correlates with the end of this period of enhanced LIP magmatism.

Another factor to consider is that there are many LIP events (averaging once every 20–30 Myr, Section 1.1), but most are not linked with iron formation, indicating other controlling factors such as oceanic composition (T. Lyons, 2016, Pers. Comm.). For instance, the Fe-flux from an oceanic plateau would needs to overwhelms the oceanic oxidation state, so that iron can be transported and deposited distally yielding iron formations (cf. Bekker et al., 2010). However, the presence of dissolved sulphate ion leads to the precipitation of iron sulphide and therefore removes Fe from the fluid and significantly reducing the contribution of Fe to the open ocean (Kump and Seyfried, 2005). So, if the ocean is sulphate-rich then even a large oceanic LIP event may not result in iron formation. This and other potential factors affecting the link between LIPs and iron formations need to be identified and modelled.

3.8.4. Cambrian explosion: burst of life at 541 Ma

The burst of life at ca. 541 Ma, the beginning of the Cambrian has been explained by a wide variety of causes including a potential stepwise burst of oxygenation (e.g. Smith and Harper, 2013; Sperling et al., 2015; Fox, 2016). Here we note that this timing is also correlated with an unusual burst of LIP pulses, collectively termed the Central Iapetus Magmatic Province (CIMP). The CIMP event is a multi-pulsed LIP event that is widespread in eastern Laurentia, Baltica and West Africa, and probably on other blocks also (Ernst and Bleeker, 2010; Youbi et al., 2016). The pulses of the CIMP event were at ca. 615, 590, 560 and 550 Ma, and probably represent more than one LIP. The environmental effects of these pulses have not been well characterized, but a broad age match with a burst of life at the beginning of the Cambrian is very suggestive of the genetic involvement of the CIMP.

4. LIPs as proxies for natural Precambrian boundaries

4.1. Lessons from the Phanerozoic record

As presented above, LIPs typically have a dramatic effect on the climate/environment and are associated with several extinction events in the Phanerozoic. Proposed kill mechanisms include global warming, oceanic anoxia, oceanic acidification, glaciations, and toxic metal input. Given the dramatic climatic/environmental impact of Phanerozoic LIP events, it is expected that Proterozoic LIPs exerted a similar major influence on the Proterozoic environment which can be monitored by excursions in the compositions in sedimentary rocks of stable isotopes such as Sr, C, O, S, Os, Mo, Cr, and through other parameters such as Hg/TOC.

4.2. Proterozoic LIP events, their links with environmental crises and utility as natural time markers

The LIP record is best understood in the Phanerozoic. However, with U-Pb dating efforts over the past 20–30 years, and particularly with a 2009–2016 industry-supported project focused on U-Pb dating of regional dolerite dyke swarms around the world (part of LIP plumbing systems) (e.g. Ernst et al., 2013) our understanding of the global Proterozoic LIP record has significantly improved (Fig. 1; for more details see Table 1.2 and Fig. 1.6 in Ernst, 2014).

LIPs can be useful as proxies for chronostratigraphically-defined Proterozoic and late Archean boundaries. Publications such as Okulitch (1987, 2002) and Bleeker (2004a, 2004b) as well as the comprehensive review by Van Kranendonk et al. (2012) have argued for a revised Precambrian time scale based on natural chronostratigraphic boundaries (in some cases correlated with LIPs) to replace the current chronometric scale (e.g. Ogg et al., 2016) that uses numbers rounded mainly to the nearest 100 Myr). In particular, Okulitch (1987, 2002) used LIP events for three Precambrian boundaries in an earlier time-scale used in Canada: For the boundary between the Meso-Helikian and Neo-Helikian in the Mesoproterozoic Okulitch (1987, 2002) chose the largest LIP event of northern Canada, the Mackenzie LIP, which extends over an area of 3 Mkm², and used the age of 1269 \pm 2 Ma from LeCheminant and Heaman (1989). In the Neoproterozoic, for the boundary between the Paleo-Hadrynian-Neo-Hadrynian, Okulitch (1987, 2002) used the second largest LIP event of northern Canada, the Franklin LIP event, which is now recognized to be even larger with its extension into southern Siberia as the Irkutsk LIP (Ernst et al., 2016a). Okulitch (2002) used the 723 \pm 3 Ma age of Heaman et al. (1990) for the boundary. Note that current dating indicates two pulses of the Franklin (+Irkutsk) LIP, one corresponding to the original ca. 723 Ma age and the other corresponding to a ca. 716 Ma age (Macdonald et al., 2010; see also Heaman et al., 1992). Finally, for the Archean–Proterozoic boundary, he used 2500 \pm 10 Ma from Heaman (1994), and this citation concerns a U-Pb age on two LIP events in southern Superior craton-Matachewan and Mistassini. So Okulitch (2002) is defining the Archean-Proterozoic boundary on the basis of the Matachewan and Mistassini LIPs. It should be noted that based on our current understanding, the Matachewan LIP is younger than 2480 Ma and the Mistassini LIP is slightly older than 2500 Ma (Hamilton, 2009).

Ideally boundaries should be placed at key events or transitions in the stratigraphic record (to establish 'golden spikes') (e.g. Gradstein et al., 2012a, 2012b; Van Kranendonk et al., 2012; Ogg et al., 2016). Given their potential to cause severe global environmental impacts, LIPs can represent proxies for such "golden spike" boundaries. As a contribution toward the identification of appropriate natural boundaries, the current Proterozoic LIP record (Ernst, 2014) is canvassed for candidates to mark such boundaries.

LIPs at 2500–2450, 2100, 2060, 1880, 1790–1750, 1525–1500, 1460, 1380, 1270, 1110, 825, 720, 615–560, 510 Ma (Table 1) are of particular significance both for their scale and extent. While, as noted in Section 3.1.4, that size is not necessarily the only factor in their potential impact on the climate, it remains an important first-order parameter. In Table 1 we compare this LIP record with the most recent version of the International Chronostratigraphic Chart by the International Commission on Stratigraphy (Ogg et al., 2016).

4.3. LIPs and Precambrian time-scales

Here we look at the current official Precambrian time scale where the boundaries are given by numbers rounded to the nearest 100 Myr (and nearest 50 Myr in the case of Rhyacian-Orosirian boundary) (Table 1) and a modified timescale (Table 2) in which more natural boundaries are used (Van Kranendonk et al., 2012; Ogg et al., 2016). In both tables we identify LIP events that would roughly match the boundaries. It should be noted that this is very provisional assessment of potential links—since the Precambrian LIP record is still poorly known, especially in terms of the overall extent of individual LIP events and their precise dating, and also in terms of the broadly correlated environmental effects (measured through sedimentary isotopic and compositional variations through time that reflect seawater and atmospheric characteristics).

5. Controls on the environmental impact of a LIP

There are several thematic aspects which further address the complexity of the relationship between LIPs and their environmental impact.

Table 1

Precambrian Period boundaries compared with selected LIPs^a.

Era	Precambrian Period	LIP event suggested to mark the "base" or "within" the Period	Comment
Neo-Proterozoic	Ediacarian (541–635 Ma)	Within: major CIMP LIP of Laurentia, Baltica & West Africa (multiple pulses ca. 615, 590, 570, 550 Ma) Youngest pulses (590–570 Ma) linked to Gaskier glaciation: Grenville dykes, Catoctin volcanics of Laurentia; Volyn LIP of Baltica (Shumlyanskyy et al., 2016a);	580 Ma Gaskiers glaciation (Section 3.2.5) linked to youngest CIMP pulse 640–635 Ma Marinoan glaciation (Section 3.2.5) no LIP
		Ouarzazate event of West African craton	link
Neo-Proterozoic	Cryogenian (635–720 Ma)	Base, at 725–715 Ma: Franklin- Irkutsk LIP of combined Laurentia and Siberia (Ernst et al., 2016a); Mutare dyke swarm of the Kalahari craton; Barangulov gabbro-granite complex in eastern Baltica (Krasnobaev et al., 2007)	720–660 Ma Sturtian glaciation (Section 3.2.5) onset linked to 725–715 Ma LIP
Neo-Proterozoic	Tonian (720–1000 Ma)	Within: Rodinia supercontinent breakup LIPs(920, 825, 780 Ma and 720 Ma) (Ernst et al., 2008; Li et al., 2008)Base, at c. 1005 Ma:Sette Daban sills of eastern Siberia (Rainbird et al., 1998)	Scale of this Sette Daban event is uncertain pending more widespread U-Pb dating
Meso-Proterozoic	Stenian (1000–1200 Ma)	Within, at 1110 Ma: Keweenawan LIP of Laurentia Umkondo LIP of Kalahari craton; Rincon de Tigre – Huanchaca LIP of Amazonia; GN (Huila) dykes of Congo craton; Mahoba dykes of Bundelkhand craton Base, at 1205 Ma: Marnda Moorn LIP of the Yilgarn craton	Scale of 1110 Ma event and presence on many blocks (<i>e.g.</i> De Kock et al., 2014) suggests significant environmental effect
Meso-Proterozoic	Ectasian (1200–1400 Ma)	Within, at 1270 Ma: Mackenzie LIP of Laurentia. Base, at 1385 Ma: Midsommerso- Zig-Zag Dal LIP of eastern Laurentia, Hart sills/volcanics & Salmon River Arch sills of western Laurentia, Mashak LIP of eastern Baltica, Chieress dykes of northern Siberia & Kunene-Kibaran LIP of Congo craton Vestfold Hills-4 dykes of East Antarctica & perhaps ca. 1380–1350 Ma event of Kalahari craton.	Scale of 1385 Ma and presence on many blocks (e.g. Ernst et al., 2008) suggest it is main breakup phases of Nuna- Columbia supercontinent and that it should have major environmental consequences
Meso-Proterozoic	Calymmian (1400–1600 Ma)	Within, at 1501 Ma: Kuonamka LIP of northern Laurentia (Ernst et al., 2016b), reconstructed with Chapada Diamantina – Curaçá dykes of Sao Francisco craton & Humpata sills of Congo craton. Within, at 1520 Ma: Essakane LIP of West Africa. Base, at 1590 Ma: Gawler Range LIP & Olympic Dam IOCG deposit of Gawler craton, reconstructed with (Hamilton and Buchan 2010) Western Channel diabase & Wernecke breccias of NW Laurentia, & Mammoth dykes of western Laurentia (Rogers et al., 2016a,b). Also Tandil dykes of Rio de la Plata craton. Base, at 1620 Ma: Melville-Bugt LIP of Greenland, Laurentia	Olympic Dam is the largest IOCG deposit
Paleo-Proterozoic	Statherian (1600–1800 Ma)	Within, at 1750 Ma: Timpton LIP of Siberia, reconstructed (Ernst et al., 2016a) with Kivallig event of Laurentia (Peterson et al. 2015). Also Tagragra of Akka dykes of West African craton, Espinhaco event of Sao Francisco craton & Vestfold Hills-3 dykes of East Antarctica. 1800–1750 Ma AMCG magmatism of Sarmatia, with two main pulses at ca. 1800 and 1750 Ma (Shumlyanskyy et al. 2016b) Base, at 1790–1780 Ma: Avanavero LIP of Amazonia, Xiong'er-Taihang LIP of the North China craton &	The interval between 1790 and 1750 Ma is a particularly dramatic time for LIP magmatism with most events concentrated in two pulses at the ends of this interval

Table 1 (continued)

Table I (continueu)		
Era	Precambrian Period	LIP event suggested to mark the "base" or "within" the Period	Comment
Paleo-Proterozoic	Orosirian (1800–2050 Ma)	Libiri dykes of West African craton. <u>Within, at 1890–1860 Ma:</u> Circum-Superior LIP of Superior craton, Mashonaland & Black Hills events of Kalahari craton (Olsson et al., 2016) & Cuddapah-Bastar LIP of greater Indian craton. Also Ghost-Mara River – Morel LIP of Slave craton reconstructed with (Ernst et al., 2016a) Kalaro-Nimnyrsky-Malodoisky event of southern Siberia (Ernst et al., 2016a).	The 1880–1870 Ma LIP pulse is associated with major pulse of iron formations Two large exogenous events occurred in this interval but did not produce LIP-scale magmatism (1850 Ma Sudbury bolide impact of southern Superior craton & 2030 Ma Vredfort bolide impact of Kaapvaal craton)
		Within, at 1980–1970 Ma: Pechenga-Onega of Karelia (Lubnina et al., 2016), Xiwangshan dykes of North China craton, Jhansi dykes of Bundelhand craton. Within, at 1998 Ma: Povunenituk- Minto-Eskimo (Kastek et al., 2016).	
		Base, at 2050–2030 Ma: Kangamiut-MD3 LIP of North Atlantic craton, Tagragra of Tata dykes of West African craton & at 2030 Ma Lac de Gras – Booth River LIP of Slave craton.	2058 Ma of major LIPs marks the end of the dramatic Lomagundi–Jatuli positive δ 13C excursion, and indeed was likely caused by these LIP events
		Base, at 2058 Ma: Bushveld LIP of Kalahari craton & Kevitsa-Kuetsjarvi-Umba LIP of Karelia craton	
Paleo-Proterozoic	Rhyacian (2050–2300 Ma)	Within, at 2125–2100 Ma: Marathon LIP of Superior craton, Indin LIP of Slave craton Bear Mountain dykes of Wyoming craton Griffin intrusions of Hearne craton)	From a LIP perspective a better choice for the base of the Rhyacian would be at 2370 Ma
		Within, at 2170–2150 Ma: Biscotasing LIP & Riviere due Gue dykes of Superior craton Wind River dykes of Wyoming craton Hengling dykes of North China craton.	
		Within, at 2190–2180 Ma: Southwest Slave Magmatic Province of Slave craton Tulemalu-MacQuoid dykes of Hearne craton Dandeli dykes of Dharwar craton	
		Within, at 2220–2210 Ma: Nipissing-Ungava LIP of Superior craton, Koli (Karjalitic) sills of Karelia, Somala dykes of Dharwar craton, Turee-Creek-Cheela Springs event of Pilbara craton, BN1 dykes of North Atlantic craton.	
		Within, at 2250 Ma: Kaptipada dykes of Singhbhum craton (Srivastava et al., 2016)	
		Base: no LIP recognized	
Paleo-Proterozoic	Siderian (2300–2500 Ma)	Within, at 2330–2320 Ma: Kuito-Taivalkovsiki event of Karelian craton (Stepanova et al., 2015).	2330 Ma new age for Great Oxidation event (Luo et al., 2016) can be linked to newly recognized to Kuito- Taivalkovsky magmatic event, of sub-LIP scale, but predicted to grow in size with additional U-Pb dating
		Within, at 2420–2370 Ma: 2420–2410 Ma Widgiemooltha LIP of Yilgarn craton 2410 Ma Sebanga Poort dykes of Zimbabwe 2400 Ma Ringvassoy dykes fragment in Norway linked to Karelian craton 2380–2410 Ma Graedefjord-Scourie LIP of North Atlantic craton 2370 Ma Bangalore-Karimnagar LIP of Dharwar craton.	
		Within, at 2480–2450 Ma: Matachewan LIP of Superior craton and reconstructed units younger pulse of Baltic LIP in Karelia-Kola, Mtshigwe dykes of Zimababwe Woongara- Weeli Wolli LIP of Pilbara craton	
		Base, at 2510–2500 Ma Mistassini LIP of Superior craton reconstructed with	

Table 1 (continued)

	Precambrian	LIP event suggested to mark the "base" or "within" the		
Era	Period	Period	Comment	
		older pulse of Baltic LIP (BLIP) of Karelia-Kola craton and with		
		Kaminak dykes of Hearne craton		
		Crystal Springs dykes of Zimbabwe		

^a Locations of LIPs in Fig. 1. Largest LIPs are included and also those with particular age correlation to known environmental effects. LIP event names **bolded**. Boundaries based on Ogg et al. (2016). LIP information from Ernst (2014) unless otherwise noted.

5.1. Differing effect of continental vs oceanic LIPs

As noted throughout this paper, there are important differences between the environmental effects of continental vs oceanic LIPs (Fig. 5). The continental LIPs primarily have a dramatic effect on atmosphere, including causing global warming, acid rain, ozone destruction, poisoning (e.g. mercury) and cooling depending on the components of gas release. Contintental LIPs also affect the marine record through the products of weathering that are transported into the ocean, and the process of weathering also reduces CO_2 in the atmosphere, leading to cooling. There is also interchange between the atmosphere and the ocean (acid rain leading to ocean acidification, contribution to anoxia conditions, fertilization leading to enhanced bio-production).

In contrast, oceanic LIPs mainly affect the marine realm (given that they remain mostly sub-aqueous), and the effect of released gases is buffered by seawater. Under favourable ocean compositions (i.e. nonsulphate rich) they can transfer metals to ocean water, potentially leading to iron formations (and manganese deposits) developing on shallow shelfs. Ocean circulation patterns which, differ according to the macroenvironmental state, Greenhouse, Hothouse, or Icehouse (Kidder and Worsley, 2010, 2012) and the sea-level (and availability of shelf space) can lead to complicated patterns of oceanic composition with depth and control the distribution of anoxia/euxinia events. In addition, oceanic plateaus can potentially contribute to cooling through enhanced productivity leading to enhanced carbon burial (D. Kidder, Pers. Comm. 2016). Kidder and Worsley (2010, 2012) suggested that geologically short Hothouse excursions, that typically last <1 Myr can be summarized as HEATT episodes, where HEATT stands for Haline Euxinic Acidic Thermal Transgression.

While our record of continental LIPs through the Proterozoic is becoming more robust (Ernst et al., 2013; Ernst, 2014), it is important to recognize that the majority of the oceanic LIP record is missing prior to about 200 Ma. No major ocean basins are preserved prior to this time and so the earlier oceanic LIPs (oceanic plateaus and ocean basin flood basalts) are only preserved as fragments in orogenic belts. About 100 oceanic LIPs are likely missing in the record back to 2.5 Ga (Dilek and Ernst, 2008); there are aspects of the anoxia and iron formation record and other environmental effects (preserved in the older sedimentary record) which must presumably be linked with this missing oceanic LIP record. Ongoing study will continue to reveal ophiolite fragments in the orogenic belts that represent former these oceanic LIPs. Further isotopic/geochemical study of the sedimentary record can potentially recognize the effects of missing oceanic LIPs and give predictions on their timing.

5.2. Uncertainty in the volume of LIP

Continental LIPs need to be better constrained in order to better predict their environmental effects and test against the observed environmental changes. It is thought that most of the continental LIPs in the Phanerozoic and Proterozoic have now been identified (Ernst et al., 2013; Ernst, 2014). However, for many of these LIPs, particularly of Proterozoic age, their overall size is unknown. As noted above the size of LIPs has an influence (although not necessarily dominant) on their environmental impact. There are two aspects to improving our understanding of the size of LIPs: 1) determining their original extent in a region and 2) tracing them between now-separated crustal blocks that were formerly adjacent (e.g. Ernst et al., 2013, 2016a, 2016b). Both aspects are more of a problem in the Proterozoic than in the Phanerozoic. In older LIPs the flood basalt component has typically been eroded and so most Proterozoic LIPs are only recognized by their exposed intrusive component (their plumbing system). Therefore, regional dating accompanied by geochemical and paleomagnetic correlation is required to determine the full distribution of intrusives (dykes, sills and layered intrusions) that belong to a LIP, and from which the original extent of the flood basalts can be estimated.

Another important aspect is the distribution of the flood basalts vs the intrusive component. It is increasing recognized (Section 3.1.3) that there are two modes of gas release in LIPs—direct release of gases from flood basalts and also gases carried to the surface via hydrothermal

Table 2

Comparison of proposed "golden spikes" (events and ages) with LIP record.^a

Age (after Van Kranendonk et al., 2012, unless noted)	Event (as described by Van Kranendonk et al., 2012, unless otherwise noted)	LIP event that can be linked
541 Ma	First appearance of Ediacaran Fauna	? youngest pulse of CIMP
630 Ma	End of Global Glaciation	? start of CIMP
720 Ma	Onset of Sturtian glaciation	Franklin-Irkutsk LIP (Laurentia-Siberia) (Ernst et al., 2016a)
850 Ma	First appearance of d13C anomalies	?
1780 Ma	First appearance of sulphidic marine deposits	Avanavero LIP (Amazonia) and coeval units (see Table 1)
2060 Ma	End of LJE (Lomagundi–Jatuli positive δ^{13} C excursion Event)/Start	Bushveld LIP (Kaapvaal) & Keivitsa-Kuetsjarvi-Umba LIP
	of shungite deposition	event (Baltica)
2250 Ma	First appearance of $+\delta^{13}$ C anomalies $+/$ or breakout magmatism	Kaptipada dykes (Singbhum)
2310–2330 Ma	2330 Ma pulse of Great Oxidation event (Luo et al., 2016)	Kuito-Taivalkovsky LIP of Karelia
c. 2430	First appearance of glacial deposits (2420 to 2440 Ma by Gumsley et al., 2017)	Last pulse of Matachewan LIP (Superior) & coeval units.
2630 Ma	First appearance Hamersley Basin BIF	?
2780 Ma	First appearance of continental flood basalts and/or positive δ^{13} C kerogen	Mount Roe-Black Range LIP (Fortescue-1) (Pilbara) &
	values	Derdepoort-Gaberone LIP (Ventersdorp-1) (Kaapvaal)
3020 Ma	First appearance of terrestrial basins	?

^a "Golden spike" information from van Kranendonk et al. (2012) and Ogg et al. (2016) and LIP record is extracted from Ernst (2014) unless otherwise noted.

vent complexes (HVCs) from the interaction of intrusives (mainly sills) with volatile-rich sedimentary rocks. The role of the intrusive component in the oceanic LIP record is unknown.

5.3. Difference between single-pulse and multi-pulse LIPs

Besides the size (volume) of LIP magmatism the other factor that is of particular significance is the duration of LIP pulses. As discussed in Section 2 there are many LIPs in which the great majority of magmatism was emplaced in an extremely short period of time on the order of a Myr or less. Examples include the 66 Ma main pulse of Deccan, the 55 Ma second pulse of the NAIP, 201 Ma CAMP, 252 Ma Siberian Traps, 259 Ma Emeishan. Such precise dating confirmed their link with mass extinctions (Section 2.1). Other less-precisely dated LIPs in the Precambrian record exhibit a single grouping of ages (to a few Myr precision) and may also represent a single short duration pulse, which should therefore be correlated with dramatic environmental changes. Examples include the 1267 Ma Mackenzie LIP, 1385 Ma Mashak (and other coeval LIPs), 1501 Kuonamka LIP, and 1755 Ma Timpton LIP (see Tables 1 and 2). Other LIPs consist of definite multiple pulses over a longer duration. The Keweenawan LIP consists of multiple pulses between 1115 and 1085 Ma with a main pulse at ca. 1100 Ma. The CIMP event is multi-pulsed between 615 and 555 Ma and its precise age structure needs to be determined for more definitive comparison with the environmental record, which just precedes the Cambrian "explosion of life". A similar observation applies to the oceanic LIP record with both single pulse and multi-pulse LIPs recognized.

All LIP events need to be dated to the same high precision (ca. <0.1 Myr) as those Phanerozoic LIPs mentioned above, with a goal to identify those Precambrian LIPs of particularly short duration which should have the greatest environmental effect. It is also critical to obtain more precise chronology of the isotopic and compositional excursions recorded in the Precambrian sedimentary record in order to more precisely compare the interpreted seawater record with LIP timing. Through such studies it will become clear which Precambrian LIPs are linked to major environmental change (warming, cooling, anoxia, acid-ification, etc.).

6. Conclusions

The rapidly accelerating research on the environmental and climatic changes in the Earth system is revealing a robust link between Large Igneous Provinces (LIPs) and major environmental catastrophes through time. In several cases LIPs with the highest precision U-Pb dating are precisely linked to mass extinction events.

LIPs are implicated directly or indirectly in a variety of environmental change mechanisms: global warming, global cooling (glaciations), anoxia, toxic gas or metal release, acid rain, ocean acidification., and stepwise oxygenation of the atmosphere. The robust linkages are particularly clear in the Phanerozoic record, but should apply to the Proterozoic and Archean record where LIPs of similar scale and frequency of occurrence are observed (averaging 20–30 Myr back to 2.5 Ga). Those largest Proterozoic LIPs are identified as potential climate changers, and in many cases match closely in time to boundaries in both the standard (Table 1) and newer "natural" (Table 2) Precambrian time scales. This suggests a role for LIPs as proxies for global environmental changes that can be recorded in the sedimentary record and marked by 'goldenspikes'.

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