Deep Carbon and the Life Cycle of Large Igneous Provinces

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arbon is central to the formation and environmental impact of large igneous provinces (LIPs). These vast magmatic events occur over geologically short timescales and include voluminous flood basalts, along with silicic and low-volume alkaline magmas. Surface outgassing of CO₂ from flood basalts may average up to 3,000 Mt per year during LIP emplacement and is subsidized by fractionating magmas deep in the crust. The large quantities of carbon mobilized in LIPs may be sourced from the convecting mantle, lithospheric mantle and crust. The relative significance of each potential carbon source is poorly known and probably varies between LIPs. Because LIPs draw on mantle reservoirs typically untapped during plate boundary magmatism, they are integral to Earth's long-term carbon cycle.

KEYWORDS: LIP, carbon, volcanism, environmental impact, atmosphere, degassing

INTRODUCTION

Large igneous provinces (LIPs) are defined as the geologically rapid emplacement (over 10^5 – 10^6 years) of hundreds of thousands to millions of cubic kilometers of lava at the surface and the associated intrusive bodies (e.g., Coffin and Eldholm 1994). They are dominated by thick successions of lavas known as flood basalts. These vast igneous provinces have formed several times throughout Earth's history, on almost all of the major continents and also in the oceans. Large igneous provinces are often found far from plate boundaries. Detailed studies of individual LIPs have shown that they are formed of igneous rocks with diverse compositions, ranging from tholeiitic basalts, to occasional rhyolites, to strongly alkaline magmas such as lamproites and carbonatites.

The generation and emplacement of LIP magmas is linked to rapid, large-scale outgassing of volatile species, including sulfur, water, halogens, and carbon dioxide [e.g., Self et al. 2006; see also the December 2005 (v1n5) issue of Elements]. This surface outgassing is facilitated by extensive subterranean magmatic plumbing systems that form important pathways for the transfer of mantle and crustal carbon to the atmosphere (e.g., Ridley and Richards 2010; Black and Manga 2017). Among magmatic gases, carbon dioxide (CO₂) is particularly vital to the life cycle of LIP magmatism and its climatic consequences (Cui et al. 2013; Jones et al. 2016). The centrality of CO₂ in the environmental perturbations that coincide with some LIPs (e.g., Courtillot and Renne 2003)—such as the Deccan Traps (India), Siberian Traps (Russia), Karoo-Ferrar (southern Africa and Antarctica, respectively), Ontong Java Plateau

2 Department of Earth Sciences University of Cambridge, UK E-mail: sally@esc.cam.ac.uk HOW DO WE KNOW LIPS RELEASE CARBON?

Water, CO_2 , sulfur, and halogens are among the most abundant constituents in volcanic gases. While some fraction of these gases is released during volcanic eruptions, the remainder may be discharged diffusely through crust, unaccompanied by volcanic eruptions. This cryptic degassing can form an important part of the overall gas release budget, especially for CO_2 (Armstrong McKay et al. 2014). Furthermore, if the establishment of lithospheric plumbing systems during the initial development of a LIP precedes the onset of flood basalt volcanism at the surface, or if intrusive magmas solidify after the last eruptions, cryptic degassing could either precede or postdate active volcanism.

Because no LIPs are forming at the present day, studies of recent, analogous, volcanic activity (e.g., Burton et al. 2013; Pfeffer et al. 2018) provide an important source of information about the release of LIP carbon. Eruptions of tholeiitic flood basalt lavas may bear similarities to present-day fissure eruptions in Hawai'i (Kīlauea Volcano) and Iceland (Laki and Holuhraun Volcanoes). The smallervolume alkaline magmas associated with some LIPs may have had similar origins to those in the East African Rift (e.g., Foley and Fischer 2018).

At sites of present-day volcanism, both eruptive and cryptic CO_2 release can be constrained through ground-based and airborne measurements (e.g., Burton et al. 2013). More direct constraints on carbon in LIP magmas can potentially be provided by petrologic and geochemical methods, but such data are scarce and require cautious interpretation. Blebs of melt trapped inside growing crystals (commonly known as "melt inclusions") can record magmatic water, CO_2 , sulfur, and halogen concentrations at the time of entrapment and prior to eruption (e.g., Self et al. 2006). However, any CO_2 that has already exsolved at the time of melt entrapment cannot be reliably reconstructed.

Basalt Group (northwestern USA), and the Central Atlantic Magmatic Province (northwest Africa, southwest Europe, northeast and southeast North America)-renders LIP-driven climate stress an important paleoclimate analog for the present-day climate. However, the origins, budget, isotopic composition, and fate of LIP carbon remain pressing and challenging questions due to the evanescence of CO₂ in carbon-saturated mafic magmatic systems (e.g., Self et al. 2006; Armstrong McKay et al. 2014; Hartley et al. 2014; Saunders 2015; Black and Manga 2017).

(Pacific Ocean), Columbia River



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Alternatively, trace element ratios such as CO_2/Nb and CO_2/Ba from un-degassed samples can be used to infer original CO_2 content for partly degassed, primitive magmas (e.g., Hartley et al. 2014). This is because Nb and Ba exhibit a similar incompatible behavior to CO_2 during mantle melting but do not degas (e.g., Rosenthal et al. 2015).

HOW MUCH CARBON DO LIP MAGMAS RELEASE?

Although all LIPs consist of a wide variety of magma types, estimates of volatile contents have mainly been derived for tholeiitic flood basalts. Estimates for carbon in flood basalts, based on volatile and trace element concentrations of melt inclusions, are summarized in FIGURE 1. Most previous estimates of the CO₂ content of flood basalts have relied on analogous, well-studied basaltic systems, such as Kīlauea and Laki, to arrive at concentrations of 0.5-0.9 wt% CO₂ in flood basalt magmas (e.g., Self et al. 2006; Saunders 2015). Given that in continental settings, flood basalt magmas may require several weight percent of dissolved water and/or exsolved CO₂ to be sufficiently buoyant to erupt through low-density felsic continental crust (Lange 2002), these CO₂ concentrations may be underestimates.

Alternative estimates of the CO₂ concentrations in flood basalt magmas have been derived from olivine-hosted melt inclusions. These are rare and typically found in primitive flood basalts, so they may not necessarily be representative of the main phase of more fractionated tholeiitic magmatism. Moreover, analyses of CO₂ in olivine-hosted melt inclusions in tholeiitic magmas (e.g., Black et al. 2014) reflect only the dissolved amount, which forms an indeterminate fraction of the total CO₂ released per km³ of magma. Thus far, measurements of CO₂ in olivine-hosted melt inclusions from flood basalts have overlooked the CO2 in shrinkage vapor bubbles (which may dominate the total CO₂ content) and so are minimum estimates. If LIP magmas reach CO₂ saturation at high pressures, CO₂ concentrations in melt inclusions represent lower limits on initial concentrations. Consequently, it is not surprising that CO₂ measurements for melt inclusions in the Siberian Traps (Black et al. 2014) (Fig. 1) are lower than the estimates for flood basalts based on measurements from Hawai'i and Iceland (Self et al. 2006; Saunders 2015).

The use of volatile/nonvolatile trace element ratios (such as CO₂/Nb and CO₂/Ba) to estimate original CO₂ concentrations must be applied with care to flood basalt magmas. This is because processes such as recharge, assimilation, and fractional crystallization in crustal magma chambers can significantly modify concentrations of strongly incompatible trace elements. Primitive high-MgO lavas, known as picrites, may sidestep this issue and thereby provide a window into initial CO₂ concentrations. Using this approach, Ba and Nb concentrations in picrites from the Siberian Traps (Sobolev et al. 2009) and the North Atlantic Igneous Province (Kent et al. 2004) suggest original melt CO₂ concentrations between 0.1 and 2 wt% CO₂. This large range for flood basalts (FIG. 1), along with the current lack of data for more alkaline magmas, emphasizes the need for further direct constraints on carbon in LIPs.

WHERE DOES LIP CARBON COME FROM?

Large igneous provinces occupy broad areal extents, up to 10^6 km^2 (Coffin and Eldholm 1994), and are widely believed to have resulted from the impingement and lateral spreading of upwelling high-temperature mantle plume heads with diameters of up to 2,000 km at the base of the lithosphere (White and McKenzie 1995). According to their site of emplacement, LIPs may be categorized as oceanic or continental. Large igneous provinces emplaced on the



Summary of CO₂ concentrations estimated for FIGURE 1 Siberian Traps and the North Atlantic Igneous Province flood basalts, based on volatile and trace element concentrations of melt inclusions. Siberian Traps melt inclusion data are from Black et al. (2014). Ratios of CO2/Nb and CO2/Ba are assumed from Rosenthal et al. (2015), applied to Nb and Ba concentrations in picrites from the Siberian Traps (Sobolev et al. 2009) and the North Atlantic Igneous Province (Kent et al. 2004). Data are plotted in ranked order. Error bars represent 2-sigma uncertainties in the CO₂/Nb and CO₂/Ba ratios. Differences in CO₂ and Nb partitioning during low degrees of partial melting (Rosenthal et al. 2015) may explain the offset between CO2 estimated from Ba vs. Nb. Carbon dioxide inferred from these trace elements reflects melting, but does not account for CO₂ loss or gain due to flushing through a saturated plumbing system. Carbon dioxide estimates for Kilauea (Hawaii, USA) (Anderson and Poland 2017) and Laki (Iceland) (Hartley et al. 2014) are shown for comparison.

continents may draw carbon from three main reservoirs: the convecting mantle, the subcontinental lithospheric mantle, and sedimentary rocks and fluids in the crust (FIG. 2). The main source of carbon for oceanic LIPs is the convecting mantle.

Carbon dioxide behaves highly incompatibly during mantle melting (e.g., Dasgupta and Hirschmann 2010), meaning that it partitions almost entirely into the melt phase. Consequently, the initial CO₂ concentrations of magmas are determined by the carbon concentration of their mantle source and by the degree of partial melting (FIG. 3). The high ³He/⁴He ratios in some LIP magmas suggest their parental melts are formed from deep-sourced, primordial material brought up in mantle plumes. In addition to primordial carbon, mantle plumes are also likely to contain carbon that has been recycled, due to subduction and subsequent entrainment of oceanic crust by the plume. However, the fate of carbon during plate tectonic recycling is not well known (e.g., Dasgupta and Hirschmann 2010; Kelemen and Manning 2015). Furthermore, while some LIP melts have incompatible trace element and Sr, Nd, Pb and Hf isotopic ratios similar to oceanic basalts, and they appear to be derived solely from a mantle plume source, the geochemistry of many LIP melts testifies to additional contributions from the overlying lithosphere (e.g., Gibson et al. 2006).

Variations in the depth and degree of melting in upwelling mantle plumes associated with flood basalts are well-established, for example, from incompatible trace element ratios that reflect the presence or absence of garnet in the residue during melting (e.g., White and McKenzie 1995; Sobolev et al. 2011). Numerical models indicate that the extent of partial melting that occurs during upwelling of mantle





FIGURE 2 Summary diagram of large igneous province (LIP) carbon fluxes (Mt C y^{-1}), isotope ratios (δ^{13} C, in units of per mil, ‰), and various types of geological reservoirs, all placed in context. The carbonatite ledge represents a major inflection in the CO₂-bearing peridotite solidus. Solid EARTH FLUX AND RESERVOIR ESTIMATES ARE AFTER DASCUPTA AND HIRSCHMANN (2010) AND KELEMEN AND MANNING (2015).

plumes is primarily controlled by the temperature of the convecting mantle and the thickness of the overlying lithosphere (e.g., White and McKenzie 1995). If the lithosphere becomes thinner through the course of LIP magmatism, due to synemplacement extension or erosion (e.g., White and McKenzie 1995; Elkins Tanton and Hager 2000), the amount of melting will be lowest at the earliest stages of plume impact and the carbon concentration in these melts will be high (FIGS. 3 AND 4) (Sobolev et al. 2011; Black and Manga 2017). Because the lithosphere is of nonuniform thickness, the amount of melting in the plume will also vary spatially at any given time, and regions of preexisting thinning or weakness will focus plume upwelling and melting (FIG. 4) (e.g., Gibson et al. 2006).



FIGURE 3 Melt fraction and bulk CO₂ concentrations govern the initial CO₂ concentration in mantle melts. The percentage of melting, also known as the "melt fraction" or "degree of melting", is expected to increase with decreasing lithospheric thickness. Curves are based on batch melting (see inset equation) and assume that CO₂ is highly incompatible during melting (Rosenthal et al. 2015). THE RANCE IN PRIMITIVE MANTLE CO₂ CONCENTRATION IS BASED ON DASCUPTA AND HIRSCHMANN (2010) AND ANDERSON AND POLAND (2017).

Thinning or removal of the subcontinental lithospheric mantle may also potentially mobilize carbon (FIGS. 4 AND 5). While this large and ancient Earth reservoir has been proposed as a major repository for volatiles-in part due to the infiltration of small-fraction, volatilerich, convecting, mantle-sourced melts over long periods of geological time-its carbon budget and isotopic composition are poorly known (Kelemen and Manning 2015; Foley and Fischer 2017). The most concentrated accumulation of carbon is likely to be either at a depth of approximately 75 km, where experimental studies have shown that there is a depression in the CO₂-bearing peridotite solidus (FIG. 4), or in regions where redox freezing traps carbon as graphite or diamonds, which can later be oxidized by percolating carbonatitic melts.

A final, but potentially important, source of carbon to LIP magmas comes from crustal fluids and sedimentary rocks (such as evaporites, coals, carbonates, and hydrocarbons) (Fig. 2). The flux of carbon from these crustal sources depends on the country rock lithologies, the input and distribution of heat, and the fraction of gases that reach the atmosphere (e.g., Ganino and Arndt 2009).

THE TEMPO OF CARBON RELEASE AND THE LIFE CYCLE OF LIPS

Large igneous provinces are commonly emplaced over several million years, but the main pulse of flood basalt volcanism occurs on timescales of a million years or less (e.g., Courtillot and Renne 2003 and subsequent geochronological studies). The flux of CO₂ is, therefore, likely to vary during LIP emplacement (FIG. 5) and through the course of individual LIP eruptions. Both the evolving CO₂ flux and δ^{13} C depend on magma emplacement rates, melting conditions, carbon sources, and flushing of CO₂ through the magmatic system as a fluid phase that is not bound to magma transfer. All of these factors are likely to shift through the life cycle of a LIP.

The tempo of magma emplacement can be constrained through studies of geochronology, physical volcanology, paleomagnetism, radiogenic isotope systems, or proxies such as mercury deposition. These lines of evidence retain significant uncertainties, but they do generally support the existence of short-timescale variations in volcanic activity superposed on gradually shifting long-term mean volcanic fluxes (e.g., Self et al. 2014 and references therein).

Geochronologic studies show that low-degree, incompatible trace element–rich, lithospheric melts often pre- and postdate the main phase outpourings of flood basalts (e.g., Gibson et al. 2006). If lithospheric removal occurs during LIP emplacement, this could also trigger a pulse of devolatilization from both the foundering lithospheric material and the residual subcontinental lithosphere under a steeper geotherm (e.g., Elkins Tanton and Hager 2000; Gibson et al. 2006) (FiG. 4). Thermomechanical transitions may modulate the depths of magma storage and, therefore, the country rock lithologies that are to be subjected to heating and devolatilization (Burgess et al. 2017); crustal metamorphism also requires heating of large volumes of rock, and outgassing from the cold upper crust may, therefore, lag behind the onset of volcanism (Black and Manga 2017).

On the timescales of individual eruptions, carbon outgassing can be decoupled from volcanic flux, for example when CO_2 partitions into a fluid phase. Ground-based measurements of the Holuhraun (Iceland) fissure eruption of 2014–2015 revealed that CO_2/SO_2 ratios in the volcanic

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1 Early phase in LIP formation



Mantle plume-lithosphere interactions through the FIGURE 4 life cycle of continental large igneous provinces (LIPs) can influence the melting regime of the convecting mantle and the subcontinental mantle lithosphere. (1) During the initial impingement of a mantle plume ('red') beneath thick continental lithosphere (yellow and brown), low-degree partial melts from metasomatised lithospheric mantle predominate (PANEL A). (2) Over the course of LIP magmatism, the lithosphere undergoes significant thinning through extension (e.g., White and McKenzie 1995; Gibson et al. 2006) and/or foundering (Elkins Tanton and Hager 2000; Sobolev et al. 2011). PANEL (C) illustrates that formation of tholeiitic basalts through adiabatic decompression melting in the mantle plume imposes a maximum lithospheric thickness during main-phase flood basalt magmatism of ~70 km. PANELS (B) AND (D) show experimentally determined solidus curves for mantle melting and reveal how the conductive thermal gradients in the lithosphere steepen at the base of the lithosphere following mantle plume impact. This conductive heating triggers low-degree melting of the lithospheric mantle and the formation of carbonated silicate melts in the late-stages of LIP formation. Abbreviations: $T_{\rm P}$ = mantle potential temperature; MBL = mechanical boundary layer. MODIFIED FROM GIBSON ET AL. (2006).

plume were higher by a factor of 10 during the earliest days of the eruption (Pfeffer et al. 2018).

Flipping the causal relationship, evolving CO₂ concentrations during fractionation of magmas in the deep crust have also been hypothesized to exert control over the eruptibility of flood basalt magmas. Carbon dioxide may, therefore, play a role in shaping the tempo of volcanic activity and outgassing (Lange 2002; Black and Manga 2017).

OUTGASSING OF LIP CARBON AND THE ROLE OF DEEP INTRUSIVE MAGMAS

The depths at which LIP magmas become saturated in an exsolved CO₂-rich phase, and the mobility and fate of the exsolved fluid, are critical to understanding their overall carbon outgassing history. The proportion of a magmatic volatile—one that is initially dissolved in the melt-that reaches the atmosphere can be thought of as the outgassing efficiency. For CO₂, it is commonly assumed that the outgassing efficiency is close to 100% for extrusive flood basalt magmas, due to the very low solubility of CO₂ in basaltic melt at 1 atmosphere pressure (e.g., Self et al. 2006). In conjunction with an assumed CO₂ content of 0.5 wt% in a primitive basaltic melt, this efficiency implies an approximate CO₂ yield of 14 Mt/ km³ erupted magma (Self et al. 2006). Importantly, if the CO₂ outgassing efficiency deviates significantly from 100%, carbon isotope fractionation due to partial degassing may shift the net δ^{13} C of the carbon that is released.

Estimates of CO₂ outgassing that are based solely on emplacement rates of flood basalts do not account for the potential flux of CO2 from associated intrusive magmas. Outgassing from CO₂ saturated magma bodies in the permeable upper crust may take place through gradual, passive degassing in conjunction with emissions during eruptions (e.g., Burton 2013). In the less permeable lower crust and lithospheric mantle, dike formation and magma ascent may provide one of the only avenues for CO2-rich exsolved fluids to reach the surface. In this case, CO₂ initially exsolved at depth

could "flush" shallower magmas, increasing CO2 release beyond what would be expected from the volume of erupted flood basalts (e.g., Armstrong McKay et al. 2014). The hypothesis of large-scale CO₂ flushing in the complex magmatic plumbing systems associated with flood basalts receives some support from studies of Icelandic fissure eruptions. Comparison between trace element concentrations and melt inclusion CO2 content from the 1783-1784 Laki (Iceland) fissure eruption suggests that ~60% of the initial CO2 cargo was degassed in the lower-to-middle crust (Hartley et al. 2014).

The importance of deep intrusive degassing depends on the relative volumes of intrusive and extrusive magmas. Based on petrology and seismic imaging of high-velocity layers near the Moho, Ridley and Richards (2010) infer that the ultramafic cumulates that may underly LIPs are comparable in volume to the erupted lavas. A range in intrusive/extrusive ratio of 0.5 to 4 implies that 30%-80% of LIP magmas do not erupt. The efficiency with which these deep intrusive magmas degas and transfer CO₂ to the atmosphere is uncertain; Hartley et al. (2014) estimated a 40-60% degassing rate of intrusive magmas in the Laki plumbing system, but this rate could be higher if crystallization in deep magma bodies drives further CO2 exsolution. Assuming homogeneous CO2 content, 50% intrusive degassing, and efficient transfer of CO₂ to the atmosphere via flushing through the magmatic system and eruption, the magmas that do erupt could carry 1.25 to 3 times their native CO₂ content assuming an intrusive/extrusive ration of 0.5 to 4. This "excess carbon" load is, in some ways, analogous to the "excess sulfur" released from some arc volcanic eruptions that tap a sulfur-rich exsolved phase (e.g., Armstrong McKay et al. 2014 and references therein).





FIGURE 5 Schematic illustration of the evolving contributions of CO_2 from the convecting mantle, mantle lithosphere, and crust during large igneous province (LIP) emplacement. (UPPER GRAPH) The degree of melting varies during the life cycle of a LIP. (LOWER GRAPH) The relative contributions and timings of CO_2 release from different reservoirs may vary from LIP to LIP. Carbon dioxide from the crust is likely to be characterized by a different carbon isotope composition than CO_2 from the mantle. The carbon isotope composition of the lithospheric mantle is uncertain. Moho = Mohorovičić discontinuity, which occurs ~8 km beneath oceanic crust and ~32 km beneath continental crust.

HOW DOES LIP CARBON INFLUENCE THE ENVIRONMENT?

The fluxes of CO_2 during LIP magmatism, and, consequently, the viability of CO_2 as a significant driver of climate change, have been the subject of debate (e.g., Self et al. 2006 and references therein; Saunders 2015; Black and Manga 2017). Perhaps the best evidence for major perturbation of the global carbon cycle by LIPs comes from carbon isotope records (see Box 1) and independent paleoclimate and pCO_2 proxies, which are discussed further in Schobben et al. (2019 this issue). In brief, these lines of evidence indicate four major aspects of carbon cycle disruption: 1) strong warming coinciding with some LIPs (e.g., the Siberian Traps and the North Atlantic Igneous

Box 1 CARBON ISOTOPE RECORDS AND MANTLE CARBON ISOTOPE RATIOS

The δ^{13} C in marine carbonates and organic matter reflects the balance between the addition and removal of carbon (with specific δ^{13} C values) to the ocean-atmosphere system. Fluctuations in δ^{13} C are, therefore, often interpreted as changes in the carbon being added to, or removed from, the oceans and atmosphere.

The isotopic composition of carbon in LIP magmas is important because the negative marine carbon isotope excursions that are recorded in marine sediments coinciding with the emplacement of some LIPs (e.g., Schobben et al. 2019 this issue). A prevalent explanation for these isotope excursions is rapid injection of large quantities of light carbon. Like CO₂ concentrations, the carbon isotope composition of flood basalt carbon is difficult to measure directly due to fractionation during degassing. Analogy with carbon from other tectonic settings implies δ^{13} C is ~ -5‰ to -8‰ in LIP magmas. Such a carbon isotope composition is too positive to explain the observed marine carbon excursions (e.g., Cui et al. 2013). However, δ^{13} C of LIP carbon release could potentially diverge from values of ~ -5% to -8%due to heterogeneous mantle carbon, fractionation in the magmatic system, or interaction with crustal carbon. For example, melting of a mantle plume component rich in recycled oceanic crust has been hypothesized as a source of isotopically light carbon (Sobolev et al. 2011). Magmatic carbon isotopes are fractionated during open-system degassing. Assimilation or heating of crustal carbon reservoirs (coals, hydrocarbons, organic-rich shales) can lead to release of very isotopically light carbon (e.g., Ganino and Arndt 2009). If multiple reservoirs contribute carbon during LIP emplacement, the δ^{13} C values, as well as the flux of carbon, may evolve through time. Thus, determining the isotope composition of carbon outgassed during LIP magmatism remains an important question for future work.

Province) (see Saunders 2015), with more ambiguous evidence in other cases; 2) spikes in atmospheric pCO_2 ; 3) negative carbon isotope excursions (e.g., Cui et al. 2013; Schobben et al. 2019 this issue); 4) ocean acidification. Taken together with geochronology aligning these environmental changes to LIP magmatism (e.g., Courtillot and Renne 2003), the most straightforward interpretation is that they were primarily caused by carbon release related to LIP emplacement, possibly supplemented with light carbon from clathrates or from the metamorphism of sedimentary organic material (Box 1). Accurately determining the CO_2 budget of diverse LIP magmas is critical to testing hypotheses regarding the causal links between magmatism, warming, and carbon cycle perturbation.

On the timescales of silicate weathering and water–rock reactions, LIPs may play an important role as carbon sinks, because CO_2 reacts with calcium and magnesium in basalts to form carbonate minerals (e.g., Jones et al. 2016; see also August 2019 issue, v15n4, of *Elements*). By analogy to mid-ocean ridge settings, where the balance between net outgassing and net sequestration of carbon is uncertain (e.g., Burton et al. 2013), the capacity for LIP carbon sequestration on longer timescales may rival the magnitude of potential outgassing (Jones et al. 2016). This balance, and the timescales of atmospheric CO_2 drawdown, may depend on the extent of subaerial versus submarine volcanism in a given LIP and the potential for water–rock reactions in hydrothermal systems.

SOME IMPORTANT QUESTIONS FOR FUTURE WORK

- 1. What is the carbon isotope composition of carbon released during LIP magmatism, and how does this relate to fractionation during degassing, interaction with carbon-bearing country rocks, and the initial composition of magmatic carbon?
- 2. What role does deep CO₂ exsolution play in regulating ascent and eruption of LIP magmas, and what fraction of CO₂ exsolved at depth reaches the atmosphere?
- 3. How do alkaline and carbonatite magmas relate to and physically interact with tholeiitic magmas, and what do alkaline magmas tell us about the influence of CO₂ and other volatiles on the petrologic evolution of LIP magmas?
- 4. How do LIPs contribute to storage and liberation of volatiles, especially carbon species, in the subcontinental lithospheric mantle?
- 5. On the 10⁵–10⁶ year timescales of silicate weathering, does LIP emplacement lead to prolonged warming, transient warming followed by cooling as silicate weathering proceeds, negligible climate change, or predominant cooling? If the long-term climatic consequences differ between LIPs, what controls these outcomes (discussed further by McKenzie and Jiang 2019 this issue)?

CONCLUSIONS

Large igneous provinces are dominated volumetrically by vast outpourings of flood basalt lavas and their intrusive equivalents. The frequent association of alkaline and carbonatite magmatism with flood basalts in LIPs attests to the petrologic importance of carbon during the generation of LIP magmas, though when and how plumbing systems associated with diverse magma types interact with each other is an unresolved question. Previous estimates of the CO₂ content of flood basalts range from 0.5 wt% to 0.9 wt% CO₂. Revised estimates of the CO₂ content of Hawaiian (Kīlauea) and Icelandic (Laki) basalts, along with incompatible trace elements from flood basalt picrites, suggest that primitive flood basalt magmas may commonly carry

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~1 wt% CO_2 or more. However, such primitive magmas comprise a small fraction of the erupted lavas. More detailed numerical models and geochemical measurements are required to understand the carbon concentrations in flood basalts and other magma types in LIPs. For example, the carbon delivery potential of voluminous tholeiite lavas in flood basalt successions is important but poorly constrained. While their parental magmas result from high degrees of partial melting and are, therefore, less likely to be intrinsically CO_2 -rich (Fig. 3), they may receive a boost from CO_2 -rich fluids released from deep intrusive magmas.

Based on the shifting contributions of deep convecting mantle, lithospheric mantle, and crustal sources (FiGs. 4 and 5), together with the variable flux from deep intrusive magmas, the CO_2 flux from LIP magmas probably evolves through the entire magmatic cycle. As a consequence, LIP carbon emissions are unlikely to scale directly with volumetric eruption rates, which offer, at best, a partial picture of the tempo of carbon outgassing. Nevertheless, gross estimates based on erupted volume provide a starting place for situating LIPs in the context of the global carbon cycle. For a total LIP magma volume of 10^6-10^7 km³ emplaced over 10^5-10^6 years, and carrying ~1 wt% CO₂,

REFERENCES

- Anderson KR, Poland MP (2017) Abundant carbon in the mantle beneath Hawai'i. Nature Geoscience 10: 704-708
- Armstrong McKay DI, Tyrrell T, Wilson PA, Foster GL (2014) Estimating the impact of the cryptic degassing of Large Igneous Provinces: a mid-Miocene case-study. Earth and Planetary Science Letters 403: 254-262
- Black BA, Hauri EH, Elkins-Tanton LT, Brown SM (2014) Sulfur isotopic evidence for sources of volatiles in Siberian Traps magmas. Earth and Planetary Science Letters 394: 58-69
- Black BA, Manga M (2017) Volatiles and the tempo of flood basalt magmatism. Earth and Planetary Science Letters 458: 130-140
- Burgess SD, Muirhead JD, Bowring SA (2017) Initial pulse of Siberian Traps sills as the trigger of the end-Permian mass extinction. Nature Communications 8, doi: 10.1038/ s41467-017-00083-9
- Burton MR, Sawyer GM, Granieri D (2013) Deep carbon emissions from volcanoes. Reviews in Mineralogy and Geochemistry 75: 323-354
- Coffin MF, Eldholm O (1994) Large igneous provinces: crustal structure, dimensions, and external consequences. Reviews of Geophysics 32: 1-36
- Courtillot VE, Renne PR (2003) On the ages of flood basalt events. Comptes Rendus Geoscience 335: 113-140
- Cui Y, Kump LR, Ridgwell A (2013) Initial assessment of the carbon emission rate and climatic consequences during the end-Permian mass extinction. Palaeogeography, Palaeoclimatology, Palaeoecology 389: 128-136
- Dasgupta R, Hirschmann MM (2010) The deep carbon cycle and melting in Earth's interior. Earth and Planetary Science Letters 298: 1-13
- Elkins Tanton LT, Hager BH (2000) Melt intrusion as a trigger for lithospheric foundering and the eruption of the Siberian flood basalts. Geophysical Research Letters 27: 3937-3940

- Foley SF, Fischer TP (2017) An essential role for continental rifts and lithosphere in the deep carbon cycle. Nature Geoscience 10: 897-902
- Ganino C, Arndt NT (2009) Climate changes caused by degassing of sediments during the emplacement of large igneous provinces. Geology 37: 323-326
- Gibson SA, Thompson RN, Day JA (2006) Timescales and mechanisms of plume– lithosphere interactions: ⁴⁰Ar/³⁹Ar geochronology and geochemistry of alkaline igneous rocks from the Paraná– Etendeka large igneous province. Earth and Planetary Science Letters 251: 1-17
- Hartley ME, Maclennan J, Edmonds M, Thordarson T (2014) Reconstructing the deep CO_2 degassing behaviour of large basaltic fissure eruptions. Earth and Planetary Science Letters 393: 120-131
- Jones MT, Jerram DA, Svensen HH, Grove C (2016) The effects of large igneous provinces on the global carbon and sulphur cycles. Palaeogeography, Palaeoclimatology, Palaeoecology 441: 4-21
- Kelemen PB, Manning CE (2015) Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. Proceedings of the National Academy of Sciences of the United States of America 112, doi: 10.1073/ pnas.1507889112
- Kent AJR and 5 coauthors (2004) Mantle heterogeneity during the formation of the North Atlantic Igneous Province: constraints from trace element and Sr-Nd-Os-O isotope systematics of Baffin Island picrites. Geochemistry, Geophysics, Geosystems 5, doi: 10.1029/2004GC000743
- Lange RA (2002) Constraints on the preeruptive volatile concentrations in the Columbia River flood basalts. Geology 30: 179-182
- McKenzie NR, Jiang H (2019) Earth outgassing and climatic transitions: the slow burn towards environmental "catastrophes"? Elements 15: 325-330
- Pfeffer MA and 32 coauthors (2018) Ground-based measurements of the 2014–2015 Holuhraun volcanic cloud

the mean annual flux would be 30-3,000 Mt CO₂/year, with the potential for orders of magnitude deviation from this mean rate over the course of the magmatic cycle. The Laki fissure eruption released an estimated 300-900 Mt CO₂ over the course of 8 months (Hartley et al. 2014). For comparison, the present-day global subaerially released flux of CO₂ from volcanoes has been estimated at 300-600 Mt CO₂/year (Burton et al. 2013; Kelemen and Manning 2015). During geologically brief intervals of intense outgassing, LIPs are likely to dominate the global flux of deep carbon to the atmosphere.

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(Iceland). Geosciences 8, doi: 10.3390/ geosciences8010029

- Ridley VA, Richards MA (2010) Deep crustal structure beneath large igneous provinces and the petrologic evolution of flood basalts. Geochemistry, Geophysics, Geosystems 11, doi: 10.1029/2009GC002935
- Rosenthal A, Hauri EH, Hirschmann MM (2015) Experimental determination of C, F, and H partitioning between mantle minerals and carbonated basalt, CO₂/Ba and CO₂/Nb systematics of partial melting, and the CO₂ contents of basaltic source regions. Earth and Planetary Science Letters 412: 77-87
- Saunders AD (2015) Two LIPs and two Earth-system crises: the impact of the North Atlantic Igneous Province and the Siberian Traps on the Earth-surface carbon cycle. Geological Magazine 153: 201-222
- Schobben M, van de Schootbrugge B, and Wignall PB (2019) Interpreting the carbon isotope record of mass extinctions. Elements 15: 331-337
- Self S, Widdowson M, Thordarson T, Jay AE (2006) Volatile fluxes during flood basalt eruptions and potential effects on the global environment: a Deccan perspective. Earth and Planetary Science Letters 248: 518-532
- Self S, Schmidt A, Mather TA (2014) Emplacement characteristics, time scales, and volcanic gas release rates of continental flood basalt eruptions on Earth. In: Keller G, Kerr AC (eds) Volcanism, Impacts, and Mass Extinctions: Causes and Effects. Geological Society of America Special Paper 505, doi: 10.1130/2014.2505(16)
- Sobolev AV, Krivolutskaya NA, Kuzmin DV (2009) Petrology of the parental melts and mantle sources of Siberian trap magmatism. Petrology 17, doi: 10.1134/S0869591109030047
- Sobolev SV and 7 coauthors (2011) Linking mantle plumes, large igneous provinces and environmental catastrophes. Nature 477: 312-316
- White RS, McKenzie D (1995) Mantle plumes and flood basalts. Journal of Geophysical Research: Solid Earth 100: 17,543-17,585

