High-Precision Geochronology of LIP Intrusions: Records of Magma–Sediment Interaction

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1811-5209/23/0019-0302\$2.50 DOI: 10.2138/gselements.19.5.302

Reconstructing the tempo and emplacement mechanisms of large igneous provinces (LIPs) and establishing potential links to environmental change and biological crises requires detailed and targeted high-precision geochronology. Contact metamorphism during LIP intrusive magmatism can release large volumes of thermogenic gas, so determining the timing of these events relative to global climate change is crucial. The most reliable age information comes from U-Pb geochronology; however, LIP mafic igneous rocks do not commonly crystallize U-bearing minerals, such as zircon or baddeleyite. Recent work has shown that U-rich minerals can crystallize in fractionated melt pockets in intrusive components of LIPs after contamination of the melt by sedimentary rocks at emplacement level. Zircon and baddeleyite from these pockets make high-precision U-Pb geochronology of LIPs possible, but these unique mechanisms add other complexities.

KEYWORDS: large igneous provinces; global climate perturbations; geochronology; melt contamination; zircon

INTRODUCTION

Many of Earth's Phanerozoic extinction events and major climate perturbations were coincident with the emplacement of large igneous provinces (LIPs), leading to the interpretation that continental flood basalt volcanism can trigger major anomalies in Earth's climate (e.g., Courtillot and Renne 2003; Green et al. 2022). Early studies investigating mechanisms behind this correlation focused on the timing and rate of volcanic outpouring as a proxy for volcanic degassing and compared them to periods of global change (e.g., Courtillot and Renne 2003). There was a paradigm shift beginning in the mid 2000s (e.g., Svensen et al. 2004), with researchers realizing the importance of the extensive subvolcanic (intrusive) record of LIPs on global climate. While both LIP eruptions and intrusions can rapidly emit massive volumes of volcanogenic gases (e.g., Capriolo et al. 2020), the emplacement of intrusions into sedimentary basins can also metamorphose organic-rich or evaporitebearing sediments (e.g., Svensen et al. 2004; Heimdal et al. 2019). In these cases, contact aureoles around LIP intrusions can produce significant volumes of thermogenic

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Davies for scale.

gases from shales and evaporites (see Deegan et al. 2023 this issue; Svensen et al. 2023 this issue), substantially adding to the impact of these provinces. Determining the age of these intrusions is required to link volatile outgassing to environmental and biotic impacts, the records of which are mostly from marine sedimentary successions. However, dating LIP intrusive events can be difficult, as mafic rocks preserved within a LIP's plumbing system and intrusions do not typically crystallize minerals commonly used in highprecision U-Pb geochronology. To assess the full impact of LIP events on the global climate, particularly the rate of change and durations

of climate perturbations, it is crucial to develop complete chronological records of LIPs and connect them to the geological climate record.

INFERRING CAUSAL RELATIONSHIPS BETWEEN LIPS AND GLOBAL CHANGE THROUGH GEOCHRONOLOGY

The history of global climate and ocean chemistry during mass extinction events is stored in the sedimentary record, which documents changes in paleo-biodiversity (colloquially termed "mass extinctions"), shifts in carbon isotopes indicative of global climate change, and evidence for anoxic or stratified oceanic depositional environments (e.g., Lindström et al. 2021; Heimdal et al. 2021). Variations of carbon isotopes or other proxies can be temporally constrained through U-Pb geochronology of zircon in ash beds contained within sedimentary successions, which bracket these events (e.g., Schoene et al. 2010). Zircon (ZrSiO₄) is a particularly good geochronologic tool for this application because it forms during late-stage crystallization of intermediate to felsic magmas, and is robust to alteration, and therefore is commonly found in ash beds intercallated throughout the sedimentary record. Zircon also readily incorporates U but little to no Pb during crystallization, allowing for particularly precise and accurate dates to be calculated from measuring the radiogenic in-growth of Pb from U decay. Zircon can also be pretreated using chemical abrasion, a technique which preferentially dissolves damaged crystallographic domains that may have lost Pb, allowing for reconstruction of an accurate temporal record of the mineral's crystallization (e.g., Widmann et al. 2019). The record of rapid climate shifts during mass extinction events preserved in sediments and temporally

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FIGURE 1 Schematic block diagram of a large igneous province (LIP), highlighting the trans-crustal nature of these magmatic events, the assembly of large volume intrusive suites in subvolcanic basins, and the potential sources of volatile gas release associated with global climate change. The grey intrusions and lava flows have solidified, whereas the orange intrusions and active lava flow are actively crystallizing. The blue arrows indicate the release of volcanogenic gases, while the green arrows indicate the

production and expulsion of thermogenic gases. The inset figure shows a simplified model of the production of thermogenic outgassing coeval with LIP sill emplacement. The abundance and volume of LIP volcanic flows and sills are not meant to be representative, nor is the relative abundance of crystalline rocks relative to magmarich intrusions or active lava flows; the entire volume of magmas associated with individual LIP events can be more than 1 Mkm³.

constrained by U-Pb dating of zircon from ash beds can be interrogated using global climate models to help understand the links between the LIP-associated degassing and climate and oceanic changes.

Large igneous provinces erupt massive volumes of lava and can crystallize significant volumes of intrusions in the crust. These intrusions are considered part of the transcrustal magmatic plumbing system that feeds flood basalts, and can be responsible for the release and generation of climate-active volatiles (FIG. 1). Throughout the ascent and solidification of LIP magmas, they can exsolve significant abundances of mantle-derived volatiles, which are introduced to the atmosphere during LIP eruptions and intrusive crystallization (e.g., CO₂, SO₂, HCl, HF; Capriolo et al. 2020; Black et al. 2021). This addition of volcanogenic volatiles to the atmosphere can be compounded by gases released from contact metamorphism of carbon-rich or evaporitic sedimentary rocks at intrusive emplacement levels (FIG. 1; e.g., Deegan et al. 2022; Svensen et al. 2023 this issue). Linking these LIP-related degassing events to mass extinctions and climate perturbations requires detailed geochronology to establish synchronicity.

There has been a lot of detailed work evaluating the timing and flux of LIP lavas, and their resulting contributions to global climate perturbations (e.g., Schoene et al. 2019; Sprain et al. 2019). However, establishing a direct link between magmatic activity, volatile degassing, and climatic effects requires an inventory of volatile output that includes the intrusive components of LIPs throughout their lifespans. As a result, it is crucial to determine the flux of the intrusive components of LIPs into the crust.

DIRECT AND INDIRECT APPROACHES TO DATING LARGE IGNEOUS PROVINCES

Developing a geochronologic record of both the intrusive and extrusive components of LIPs is required to interpret their global impact on the atmosphere and biosphere. Unfortunately, dating LIPs presents a significant challenge, as these provinces are dominated by mafic rocks and do not commonly contain the mineral phases used for high-precision geochronology. Generally, most high-precision geochronology datasets utilize either U-Pb zircon or 40Ar/39Ar (hereafter "Ar-Ar") K-feldspar geochronology. However, mafic rocks are commonly zircon undersaturated, and feldspars crystallizing from these magmas are typically K-poor, Ca-rich plagioclase, which leads to low abundances of radiogenic ⁴⁰Ar and analytical challenges due to elevated Ca contents. As a result of these limitations, some recent studies have utilized an indirect approach to determining the timing and duration of LIP eruptions by dating silicic volcanic horizons interbedded within flood basalts.

Unfortunately, most flood basalt successions lack the coeval local silicic volcanism required to deposit zircon-bearing ash between basalt flows (e.g., Marzoli et al. 2018; Antoine et al. 2022). Furthermore, ash horizons cannot be used to date the intrusive component of LIPs (e.g., Black et al. 2021). Previous work has attempted to correlate well-dated intrusive components of LIPs with extrusive phases using geochemical proxies (e.g., Blackburn et al. 2013). However, this approach has several drawbacks, as it requires a clear geochemical link between different intrusions and their eruptive counterparts, which can be located 1000s of kilometers apart, and regionally restricted LIP lavas can have unique compositions (e.g., Marzoli et al. 2018). As a result, it is preferable to directly date all components of LIPs, when possible, to build complete datasets for the full assembly of LIPs, which can then be compared to the timing of environmental disturbances and mass extinctions recorded in the sedimentary record. Furthermore, due to the tremendous size of LIPs, spatial age variations must also be investigated.



The most common geochronologic system used to directly date LIP lava flows has been plagioclase feldspar Ar-Ar geochronology. Feldspar is ubiquitous in silicate rocks and the decay of ⁴⁰K to ⁴⁰Ar within feldspars allows direct dating of rapidly cooled mafic rocks (e.g., Jiang et al. 2023). However, the K-Ar system in plagioclase may be disturbed through thermally-driven diffusion of radiogenic Ar, as high-temperature alteration can reset Ar isotope systematics to dates younger than crystallization (e.g., Antoine et al. 2022). Furthermore, plagioclase can be altered during later, lower-temperature hydrothermal events, which recrystallize zones of the crystal lattice and create secondary mineral inclusions, further biasing Ar-Ar age determinations away from the timing of crystallization (Antoine et al. 2022). Thermogenic gases and hydrothermal fluid circulation cells generated by the intrusion of LIP dike and sill networks into the upper crust may cause both fluid-overprinting of distal host rocks and directly alter the minerals of the mafic rocks. As a result, it is likely that the Ar-Ar geochronologic record of LIP emplacement and associated volatile degassing may not accurately record the timing of crystallization.

In some cases, an alternative to avoid the potential inaccuracies of the Ar-Ar system is use of the U-Pb system in zircon (ZrSiO₄) and baddeleyite (ZrO₂), both of which readily incorporate U into their crystal structure during crystallization while excluding Pb, making them ideal for U-Pb geochronology. The type of zirconium-bearing mineral that crystallizes from a magma is controlled by many factors, including the melt composition, oxygen fugacity, and water content. Due to the relatively dry and SiO₂-poor nature of mafic LIP melts, they are likely to reach baddeleyite saturation through fractional crystallization before zircon (e.g., Schaltegger and Davies 2017). As a result, baddeleyite frequently has been used to develop high-precision geochronology for LIP intrusions (e.g., Jiang et al. 2023). While baddeleyite can generate high-precision U-Pb dates, it may be susceptible to alteration from hydrothermal events (e.g., Davies et al. 2018) and can accumulate radiation damage due to the radioactive decay of structurally bound U and Th, although it is more resistant to such processes than zircon (Schaltegger and Davies 2017). However, the main drawback of baddeleyite U-Pb geochronology is that the chemical abrasion technique, which is effective in removing altered domains and improving the accuracy of zircon U-Pb dates, does not work for baddeleyite (e.g., Rioux et al. 2010).

ZIRCON CRYSTALLIZATION IN LIP MAGMAS

Zircon can crystallize in LIP magmas under certain conditions. It is most frequently found in intrusions and occasionally in flows (e.g., Schoene et al. 2010; Blackburn et al. 2013; Burgess et al. 2015a, 2017). In some hydrous felsic melts, zircon can contain multiple growth domains, representing previous generations of zircon crystallization and complicating age interpretations. However, in mostly dry mafic LIP magmas, zircon generally does not crystallize until the final stages of crystallization at relatively low temperatures (e.g., Davies et al. 2021). The basaltic composition of LIP melts also makes them less likely to preserve zircon xenocrysts entrained early in the melt's history. Therefore, theoretically, zircon found in LIP samples should form directly from a highly evolved, silica-rich liquid just before final solidification and U-Pb ages from these zircon crystals should serve as a robust tie point for developing a high-precision chronology of solidification of that LIP unit.

The most successful sampling targets for zircon from mafic LIP rocks have been coarse-grained, felsic segregations, commonly observed as pods or veins, interfingered within more fine-grained rocks (FIG. 2). Based on their compositions, they have been interpreted to represent the late-stage coalescence of evolved interstitial melt from within larger mafic host rocks (e.g., Burgess et al. 2015b). For example, coarse-grained segregations from both intrusive and extrusive rocks from the Jurassic Ferrar LIP in Antarctica and Tasmania yielded zircon with largely internally consistent and precise age spectra, as expected from rapid cooling and crystallization, indicating that the intrusive and extrusive phases of magmatism occurred over an interval of 349 ± 49 ky (Burgess et al. 2015a). Intrusions from the Permian-Triassic Siberian Traps LIP in Russia also yielded zircon age spectra without discernable spread in dates within individual samples, interpreted as rapid cooling and crystallization of LIP zircon (Burgess et al. 2017). These ages also indicate that the emplacement of laterally extensive sills throughout the basin and resulting thermogenic degassing occurred coeval with the end-Permian boundary, interpreted as indicating that this phase of LIP magmatism was likely responsible for the Earth's most severe mass extinction (Burgess et al. 2017).

Despite the success of these examples, and other studies using zircon from intrusive samples to constrain the age of LIP emplacement (e.g., Blackburn et al. 2013; Burgess et al. 2015a, 2017; Davies et al. 2017; Gaynor et al. 2022), most well-studied volcanic components of LIPs, such as the Central Atlantic Magmatic Province (CAMP), Columbia River Basalts, Deccan Traps, and Karoo LIPs contain little to no zircon, despite extensive sampling campaigns (e.g., Kasbohm and Schoene 2018; Schoene et al. 2019; Antoine et al. 2022). This lack of zircon from many volcanic rocks suggests that crystallization of zircon from evolved interstitial horizons may not be a common mechanism. Mafic lavas and shallow intrusions of LIPs rapidly crystallize upon emplacement, solidifying on the time frame of 10s to 1000s of years (e.g., Heimdal et al. 2021), which may be too short to facilitate late-stage crystallization of accessory phases like zircon; and when present, they may be too small to analyze. Mafic magmas require protracted cooling to sufficiently fractionate to zircon saturation; rapid cooling may not allow for the generation of an evolved interstitial liquid with the lifespan necessary for zircon nucleation and growth.

Recent zircon U-Pb geochronology studies have focused on coarse-grained portions of LIP intrusions from the Karoo and CAMP and have shown U-Pb age variations larger than expected based on cooling timescales from simple thermal models (e.g., Davies et al. 2021; Gaynor et al. 2022). For zircon to yield U-Pb dates beyond what is possible for the cooling in the upper crust, an additional mechanism must be driving these protracted dates. Isotope data and geochronological evidence from pegmatitic pods suggest that they crystallized during contamination near the emplacement level. Therefore, the presence of zircon within the coarse-grained portions of many LIP sills may represent a contamination process during the evolution of these broader systems and holds additional insight into their emplacement.



FIGURE 2 Field and mineralogical characteristics of coarsegrained enclaves within LIP samples, showing the variations in coarse-grained features observed between the (**A**) North Mountain basalt in Nova Scotia Canada from the CAMP, (**B**) sills from the Wrangellia flood basalt province in Vancouver Island, Canada, and (**C**) the Karoo LIP sills located in Eastern Cape, South Africa; and examples of (**D**) optical and (**E**) SEM imagery of low-Ti sills from the CAMP in Brazil and (**F**) Zr-bearing minerals from pegmatitic enclaves from the Karoo LIP. The coarse-grained segregations tend to be interfingered within fine-grained mafic intrusions, ranging from globular to vein-like and vary in grain-size. Baddeleyite from these enclaves (**D**) are pale brown with a distinct

EMPLACEMENT LEVEL CONTAMINATION OF LIP INTRUSIONS

Detailed geochemical studies have revealed that emplacement-level contamination is common in localized areas within LIP mafic intrusions, through melted wall rock mixing with mafic magmas (e.g., Heimdal et al. 2019). Typical whole rock isotopic compositions (Sr, Nd, Pb) of LIP lavas and intrusive rocks do not usually suggest significant emplacement-level contamination, indicating that these effects are localized. Due to these observations and new zircon geochronology and geochemistry from CAMP and Karoo LIP intrusions, recent work has suggested the presence of zircon in mafic LIP intrusions is the result of emplacement-level contamination during magma crystallization (e.g., Davies et al. 2021; Gaynor et al. 2022). During sill inflation, local fracture networks develop and introduce xenolith blocks of wall rock into the hot, mafic magma. These blocks can then be entrained in the passing magma and rapidly dissolve (FIG. 3). As the flux of magma into the intrusion slows, isolated blocks of wall rock dissolve in place and locally introduce Si, Al, and other cations impor-

cleavage and often show single terminations, zircon (**E**, **F**) tends to be fractured and lacking its characteristic habit. The internal structures revealed by SEM and CL imagery largely lack the oscillatory or sector zoning common in zircon; instead, they show a strongly reduced CL response due to metamict crystal structure. Some crystals host growth zones indicative of growth during rapid shifts in melt compositions and abundant inclusions. In (**B**) and (**C**), the interpreted margins of coarse-grained enclaves are highlighted with dashed orange lines. The blue hilt of a rock hammer is scale for (**B**). THE SEM AND CL IMAGERY IN (**F**) IS FROM SAMPLE K08-13 FROM GAYNOR ET AL. (2022).

tant for zircon saturation, as well as Zr and volatiles (mainly H₂O). The dissolving xenoliths can also contain zircon, which should rapidly dissolve. Depending on the local melt conditions, the dissolving zircon xenocrysts can also serve as nucleation points for subsequent zircon growth, although these crystals may have xenocrystic cores and yield dates older than the intrusion. This local contamination serves as a mechanism to allow for zircon crystallization from magmas previously unable to saturate zircon. Zircons forming from these melts are hybridized between the fractionated LIP mafic melt and the dissolved assimilant geochemistry, yielding geochemical signatures that reflect this process (e.g., trace elements, Hf and O isotopes), recording compositions diverging from those generated from crystallization purely from a fractionated mafic melt (Davies et al. 2021; Gaynor et al. 2022).



FICURE 3 Schematic model highlighting the process of LIP contamination at the emplacement level, from (**A**) initial LIP sill emplacement with diking and stoping of wall-rock blocks, (**B**) wall-rock block melting during contact aureole development, and finally (**C**) crystallization of the LIP sill with final thermogenic production with coeval crystallization of coarse-

Evaluating the Extent of Local Contamination of LIP Sills Through Zircon

While upper crustal contamination may allow for localized zircon saturation, it is important to understand the extent of assimilation in these sills and the effects this has on their zircon compositions. Recent work on a suite of Jurassic Karoo LIP sills that were emplaced into the shale-bearing Ecca Group of the Karoo Basin suggested that emplacement-level contamination was responsible for the unique compositions and ages of the zircon found in these rocks. Zircon dates from pegmatitic pods mostly clustered tightly around the Jurassic age of the LIP, although individual dates were both anomalously younger and older, including Archean dates. The older portion of these age spectra can be explained by xenocrystic ancient detrital zircon material from the ingested clastic sediment, while the anomalously younger ages are likely an analytical artifact resulting from the composition of zircon crystallized in these pods. Chemical abrasion pretreatment preferentially dissolves damaged zircon domains, but the zircon crystals from these pods have U concentrations ranging up to over 10,000 ppm, well above normal values for zircon. As a result, zircon crystals from Karoo LIP sills contain abundant crystallographic damage due to the radioactive decay of U, which makes them prone to rapid dissolution during chemical abrasion. Such zircon cannot undergo the standard conditions of pretreatment and may yield U-Pb dates biased towards younger values due to the enhanced levels of radiation damage. The high U concentrations are likely the result of fluxing with brines derived from stratiform U deposits within the basin during crystallization (e.g., Le Roux 1993). Despite significant variations in U-Pb dates, the Hf isotope compositions of zircon from individual pegmatitic pods largely overlap within uncertainty, with significant differences between pods (FIG. 4). These melt pods therefore represent localized contamination, driven by significant changes in local melt composition, rather than the nucleation of new zircon onto preexisting zircon introduced during melting of sedimentary wall rock (FIG. 4). The chemical compositions of these zircon reveal extensive magma-sediment interactions at the emplacement level within Karoo LIP sills, recording the processes responsible for thermogenic degassing associated with sill emplacement.

grained enclaves. The blue arrows indicate reactions associated with the release of volcanogenic gases, while the green arrows indicate the production and expulsion of thermogenic gases. No scale is implied. THIS MODEL IS BASED ON WORK PRESENTED IN DAVIES ET AL. (2021), GAYNOR ET AL. (2022), AND DEEGAN ET AL. (2022).

Zircon Crystallization Through Contamination: A Blessing and a Curse

Forming zircon through emplacement-level contamination of LIP sills can yield complicated U-Pb age spectra, where not all dates accurately reflect sill emplacement. The inclusion of xenocrystic zircon within pods of LIP intrusions adds a significant bias away from the age of crystallization towards older ages. Further, due to high U (and Th) contents, many of the zircon crystallizing from these highly evolved contaminated melts may have elevated levels of radiation damage, facilitating Pb diffusion and hydrothermal alteration. All of these processes drive loss of radiogenic Pb. The extensive radiation damage limits the efficiency of the chemical abrasion pretreatment, so the presence of residual unmitigated Pb-loss within their age spectra requires more careful interpretation (e.g., Davies et al. 2021; Gaynor et al. 2022).

Despite these problems, the presence of zircon in some LIP intrusions provides a unique opportunity to study the climate impact of LIPs. Because zircon crystallizes during wall rock interaction, it may directly record the timing of thermogenic degassing during sill emplacement. While initial contact metamorphism, and subsequent contact aureole degassing, may occur prior to zircon saturation, the potentially short thermal lifespans of these intrusions in the upper crust may mean that the uncertainties of zircon dates encompass the timeframe of generating thermogenic gases. Comparing geochronological datasets from these intrusions with periods of global climate perturbations is an excellent test to assess the potential impact of thermogenic gas release due to metamorphism by LIP intrusions. Geochronology from the Karoo, Siberian Traps, and CAMP LIPs all suggest that sills in sedimentary basins linked with significant thermogenic volatile release have ages that overlap with the timing of carbon isotope excursions in the sedimentary record (e.g., Burgess et al. 2017; Davies et al. 2017; Gaynor et al. 2022). These carbon isotope excursions have been interpreted as originating from a mixture of LIP-driven volatile gas emissions and carbon associated with feedbacks from the biosphere related to severe climate change and degradation of environmental conditions. The presence of zircon within LIP sills is likely variable throughout the geologic record, as not all LIPs intrude large sedimentary basins. This style of contamination may be restricted to LIPs with the ability to interact



FIGURE 4 Baddeleyite and zircon U-Pb geochronology and Hf isotope geochemistry from pegmatitic pods from Karoo LIP sills emplaced into the shale-bearing Ecca Group, illustrating the significant compositional range of these crystals. The composition of the mantle source for the mafic sills is estimated at ϵ Hf = 0 (dashed line), while older crustal components present in the basin should have much more negative and variable ϵ Hf values. The inset box indicates the anticipated spread in ϵ Hf values between crystals from individual samples, several pods have very negative

with sedimentary rocks, and, thus, U-Pb zircon geochronology in LIPs rocks may be uniquely able to provide time constraints on magma–sediment interactions and potentially climatic perturbations.

BROADER IMPLICATIONS OF EMPLACEMENT LEVEL CONTAMINATION

The effects of mafic intrusions from LIPs into upper crustal basins are recorded through a variety of features, such as fracturing of wall rock, sediment fluidization structures, contact metamorphism, and breccia pipes (e.g., Deegan et al. 2023 this issue; Svensen et al. 2023 this issue). These features are the direct result of magma-sediment interactions, as are pegmatitic pods formed by emplacement-level contamination, allowing for a precise time constraint on thermogenic degassing. These structures serve as geologic capsules of magma-sediment interaction, capturing information on the composition and timing of basinal brines fluxes through intrusions and melting and deformation of wall rock. Recent work has found this style of contamination is associated with assimilation of shale or shale-bearing wall rock (e.g., Davies et al. 2021; Gaynor et al. 2022), but further work is needed to determine what amount of contamination occurs during interaction with the wall rock. The ability to tie the chronology available from these local magma contaminations to global climatic perturbations would also be bolstered by detailed study of the volatile species present within these pods (Heimdal et al. 2019).

While pegmatitic pods (and associated zircon crystallization) are the result of local contamination, understanding the full impact of the intrusive component of LIPs on the environment would require dating huge numbers of intrusions. The intrusive components of LIPs can represent EHf values, indicative of significant overprinting through crustal contamination. Baddeleyite, which should crystallize prior to zircon, yields overlapping EHf values with the zircon sampled from the same pegmatitic pod. This suggests that they represent zirconium-bearing phases growing in regions of localized contamination, driven by significant changes in local melt composition, rather than the nucleation of new magmatic zircon onto preexisting zircon introduced from melting of sedimentary wall rock. The symbol colors relate to samples, and symbol shapes indicate if the analyzed crystal was zircon (Zr) or baddeleyite (Bd). MODIFIED FROM GAYNOR ET AL. (2022).

over 100,000 km³ of mafic magmas. Therefore, building full records of intrusive LIP magmatism will require large datasets, combining geochronology with isotopic characterization of minerals within these contaminated pods, such as apatite, to better understand the extent of magma-sediment interactions between and within basins. With a temporally and spatially constrained framework, accurate degassing models can be used to inform coupled atmospheric-ocean global climate models, allowing us to gain insights into the feedback mechanisms during LIP emplacement leading to climate change and mass extinctions. Before these modeling approaches can be confidently applied, future work tying detailed chronologic records of climate change and intrusive LIP emplacement is needed to better investigate the potential causal relationships between the two. These data are needed to establish whether LIP intrusive magmatism is responsible for major atmospheric shifts, or if discrete periods of intrusions proximal to particularly volatile-rich wall rock are necessary for global climate perturbations.

ACKNOWLEDGMENTS

The ideas in this paper were formulated over several years during work funded by the Swiss National Science Foundation (projects 162341 and 182007). The authors recognize the contributions of many colleagues, including Clémentine Antoine, Andrea Boscaini, Nicolas Greber, Thea Heimdal, Andrea Marzoli, and Henrik Svensen. We also acknowledge a long list of research not cited here. This paper was significantly improved by reviews by Lars Augland and Jennifer Kasbohm and editorial comments from Sara Callegaro and Frances Deegan. This publication was supported by the Princeton University Library Open Access Fund.

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REFERENCES

- Antoine C and 5 coauthors (2022) ⁴⁰Ar/³⁹Ar geochronology of the Drakensberg continental flood basalts: understanding large argon isotopic variations in mafic groundmass and plagioclase size fractions. Chemical Geology 610: 121086, doi: 10.1016/j.chemgeo.2022.121086
- Black BA, Karlstrom L, Mather TA (2021) The life cycle of large igneous provinces. Nature Reviews Earth & Environment 2: 840-857, doi: 10.1038/s43017-021-00221-4
- Blackburn TJ and 8 coauthors (2013) Zircon U-Pb geochronology links the End-Triassic extinction with the Central Atlantic Magmatic Province. Science 340: 941-945, doi: 10.1126/science.1234204
- Burgess SD, Bowring SA, Fleming TH, Elliot DH (2015a) High-precision geochronology links the Ferrar large igneous province with early-Jurassic ocean anoxia and biotic crisis. Earth and Planetary Science Letters 415: 90-99, doi: 10.1016/j.epsl.2015.01.037
- Burgess SD, Blackburn TJ, Bowring SA (2015b) High-precision U-Pb geochronology of Phanerozoic large igneous provinces. In: Schmidt A, Fristad K, Elkins-Tanton L (eds), Volcanism and Global Environmental Change. Cambridge University Press, Cambridge, pp 47-62
- 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: 164, doi: 10.1038/s41467-017-00083-9
- Capriolo M and 13 coauthors (2020) Deep CO₂ in the end-Triassic Central Atlantic Magmatic Province. Nature Communications 11: 1670, doi: 10.1038/ s41467-020-15325-6
- Courtillot VE, Renne PR (2003) On the ages of flood basalt events. Comptes Rendus Geoscience 335: 113-140, doi: 10.1016/ s1631-0713(03)00006-3
- Davies JHFL and 5 coauthors (2017) End-Triassic mass extinction started by intrusive CAMP activity. Nature Communications 8: 15596, doi: 10.1038/ ncomms15596
- Davies JHFL and 5 coauthors (2018) Evaluating baddeleyite oxygen isotope analysis by secondary ion mass spectrometry (SIMS). Chemical Geology 479: 113-122, doi: 10.1016/j. chemgeo.2018.01.002
- Davies JHFL and 13 coauthors (2021) Zircon petrochronology in large igneous provinces reveals upper crustal contamination processes: new U–Pb ages, Hf and O isotopes, and trace elements from

the Central Atlantic magmatic province (CAMP). Contributions to Mineralogy and Petrology 176: 9, doi: 10.1007/ s00410-020-01765-2

- Deegan FM and 12 coauthors (2022) Magma-shale interaction in large igneous provinces: implications for climate warming and sulfide genesis. Journal of Petrology 63: egac094, doi: 10.1093/ petrology/egac094
- Deegan FM, Callegara S, Davies HFL, Svensen HH (2023) Driving global change one LIP at a time. Elements 19: 269-275
- Gaynor SP, Svensen HH, Polteau S, Schaltegger U (2022) Local melt contamination and global climate impact: dating the emplacement of Karoo LIP sills into organic-rich shale. Earth and Planetary Science Letters 579: 117371, doi: 10.1016/j. epsl.2022.117371
- Green T, Renne PR, Keller CB (2022) Continental flood basalts drive Phanerozoic extinctions. Proceedings of the National Academy of Sciences 119: e2120441119, 10.1073/pnas.2120441119
- Heimdal TH and 5 coauthors (2019) Evidence for magma–evaporite interactions during the emplacement of the Central Atlantic Magmatic Province (CAMP) in Brazil. Earth and Planetary Science Letters 506: 476-492, doi: 10.1016/j.epsl.2018.11.018
- Heimdal TH, Goddéris Y, Jones MT, Svensen HH (2021) Assessing the importance of thermogenic degassing from the Karoo Large Igneous Province (LIP) in driving Toarcian carbon cycle perturbations. Nature Communications 12: 6221, doi: 10.1038/s41467-021-26467-6
- Jiang Q, Jourdan F, Olierook HKH, Merle RE (2023) An appraisal of the ages of Phanerozoic large igneous provinces. Earth-Science Reviews 237: 104314, doi: 10.1016/j.earscirev.2023.104314(
- Kasbohm J, Schoene B (2018) Rapid eruption of the Columbia River flood basalt and correlation with the mid-Miocene climate optimum. Science Advances 4: eaat8223, doi: 10.1126/sciadv.aat8223
- Le Roux JP (1993) Genesis of stratiform U– Mo deposits in the Karoo Basin of South Africa. Ore Geology Reviews 7: 485-509, doi: 10.1016/0169-1368(93)90012-n
- Lindström S and 8 coauthors (2021) Tracing volcanic emissions from the Central Atlantic Magmatic Province in the sedimentary record. Earth-Science Reviews 212: 103444, doi: 10.1016/j. earscirev.2020.103444

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- Marzoli A and 9 coauthors (2018) The Central Atlantic Magmatic Province (CAMP): a review. In: Tanner LH (ed) The Late Triassic World. Topics in Geobiology, Volume 46. Springer, Cham, pp 91-125, doi: 10.1007/978-3-319-68009-5_4
- Rioux M, Bowring S, Dudás F, Hanson R (2010) Characterizing the U–Pb systematics of baddeleyite through chemical abrasion: application of multi-step digestion methods to baddeleyite geochronology. Contributions to Mineralogy and Petrology 160: 777-801, doi: 10.1007/ s00410-010-0507-1
- Schaltegger U, Davies JHFL (2017) Petrochronology of zircon and baddeleyite in igneous rocks: reconstructing magmatic processes at high temporal resolution. In: Kohn M, Engi M, Lanari P (eds) Petrochronology (Methods and Applications). Reviews in Mineralogy and Geochemistry, Volume 83. Mineralogical Society of America, Chantilly, pp 297-328, doi: 10.2138/rmg.2017.83.10
- Schoene B and 6 coauthors (2019) U-Pb constraints on pulsed eruption of the Deccan Traps across the end-Cretaceous mass extinction. Science 636: 862-866, doi: 10.1126/science.aau2422
- Schoene B, Guex J, Bartolini A, Schaltegger U, Blackburn TJ (2010) Correlating the end-Triassic mass extinction and flood basalt volcanism at the 100 ka level. Geology 38: 387-390, doi: 10.1130/ g30683.1
- Sprain CJ and 5 coauthors (2019) The eruptive tempo of Deccan volcanism in relation to the Cretaceous-Paleogene boundary. Science 363: 866-870, doi: 10.1126/science.av1446
- Svensen and 6 coauthors (2004) Release of methane from a volcanic basin as a mechanism for initial Eocene global warming. Nature 429: 542-545, doi: 10.1038/ nature02566
- Svensen HH, Jones MT, Mather TA (2023) Large igneous provinces and the release of thermogenic volatiles from sedimentary basins. Elements 19: 282-288
- Widmann P, Davies JHFL, Schaltegger U (2019) Calibrating chemical abrasion: its effects on zircon crystal structure, chemical composition and U-Pb age. Chemical Geology 511: 1-10, doi: 10.1016/j. chemgeo.2019.02.026