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**Carbonatites as a record of the carbon isotope composition
of large igneous province outgassing**

By

Ellen Gales

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Geology
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Abstract

Large igneous province (LIP) eruptions have been linked in some cases to major perturbations of Earth's carbon cycle. However, few observations directly constrain the isotopic composition of carbon released by LIP magmas because carbon isotopes fractionate during degassing, which hampers understanding of the relative roles of mantle versus crustal carbon reservoirs. Carbonatite magmatism associated with LIPs provides a unique window into the isotopic systematics of LIP carbon because the majority of carbon in carbonatites crystallizes rather than degassing. Here, we present new $\delta^{13}\text{C}$ data for the Guli carbonatites in the Siberian Traps. In addition, we compile ~260 published measurements of $\delta^{13}\text{C}$ from carbonatites related to the Deccan Traps and the Paraná-Etendeka. We find no evidence for magmas with carbon isotope ratios lighter than depleted mantle values of $\delta^{13}\text{C} = -6 \pm 2\text{‰}$ from any of these LIPs, though some carbonatites range to heavier $\delta^{13}\text{C}$ ratios. We attribute relatively heavy $\delta^{13}\text{C}$ ratios in some carbonatites to either slightly ^{13}C -enriched domains in the mantle lithosphere or carbon isotope fractionation in deep, carbon-saturated LIP magma reservoirs. The absence of a light $\delta^{13}\text{C}$ component in LIP magmas supports the view that lithospheric carbon reservoirs must be tapped during cases of LIP magmatism linked with negative carbon isotope excursions and mass extinctions.

Table of Contents

1. Introduction.....	1
2. Geologic Setting.....	3
2.1 Large Igneous Provinces.....	3
2.2 Carbon isotope excursions	4
2.3 The Guli massif (Siberian Traps), the Deccan Traps, and Paraná-Etendeka Traps.....	5
3. Methods.....	8
4. Results.....	10
5. Discussion	12
5.1 The fidelity of carbonatites and their relationship with other LIP magmas	12
5.2 The evolution of carbon in the mantle lithosphere on geologic timescales.....	13
5.3 Carbonatite outgassing and broader implications of LIP outgassing for carbon isotope excursions	15
6. Conclusions.....	16
References.....	18
Tables and Figures	24

1. Introduction

Mounting evidence links some continental large igneous provinces (LIPs) with major ocean anoxic events or mass extinctions, often marked by climate warming and carbon isotope excursions (Bachan and Payne, 2016; Burgess and Bowring, 2015; Joachimski et al., 2012; Petersen et al., 2016; Schoene et al., 2019). However, in some cases, such as the Paraná-Etendeka LIP, there are no obvious effects of magmatism on the carbon cycle. Consequently, the precise relationship between LIP magmatism and carbon cycle perturbation remains uncertain. From measurements of mantle xenoliths, carbonatites, volcanic gases, kimberlite carbonate, and carbon-rich mid-ocean ridge ‘popping rocks’ (CO₂ rich rocks dredged from mid-ocean ridges that ‘pop’ when they arrive on deck due to decompression), the overall carbon isotope composition of Earth’s mantle is thought to be $\delta^{13}\text{C} = -6 \pm 2\text{‰}$ (Deines, 2002; Javoy et al., 1986; Javoy and Pineau, 1991; Pineau and Javoy, 1983). This range of values is too heavy to plausibly explain the observed negative carbon isotope excursions through volcanic outgassing. An isotopically lighter carbon-bearing subpopulation ($\delta^{13}\text{C} \approx -20\text{‰}$) has been identified among mantle rocks and diamonds (Cartigny et al., 2014; Deines, 2002), raising the possibility of heterogeneous mantle carbon isotope ratios. Indeed, an eclogitic recycled component in the Siberian Traps plume source with $\delta^{13}\text{C} \approx -12\text{‰}$ has been invoked to link magmatism with the carbon isotope excursion that marks the onset of the end-Permian mass extinction (Sobolev et al., 2011). Similarly, light mantle carbon, perhaps mobilized from the mantle lithosphere during emplacement of the Central Atlantic Magmatic Province, has been hypothesized to explain carbon isotope records during the end-Triassic (Paris et al., 2012). Alternative hypotheses to explain carbon isotope excursions linked to volcanism involve release of light carbon from

metamorphism of carbon-bearing sedimentary rocks or from clathrate dissociation triggered by volcanogenic warming (Black et al., 2018; Gutjahr et al., 2017; Heimdal et al., 2018; Svensen et al., 2009). Determining the carbon isotope composition of large igneous province outgassing is thus central to understanding the source of the carbon that caused carbon isotope excursions and that may have played a key role in perturbing ecosystems during some emplacement of some LIPs. However, because magmatic degassing strongly fractionates carbon isotope ratios (e.g. Gerlach and Taylor, 1990), and because carbon saturation and degassing can begin deep in the magmatic system (Black and Manga, 2017; Karlstrom and Richards, 2011), the carbon isotopic composition of flood basalt magmas has remained conjectural (Saunders, 2016).

Highly carbonate-rich igneous rocks known as carbonatites offer a window onto the isotopic composition of carbon from large igneous provinces. Carbonatites from rift settings have been used to assess mantle carbon isotope systematics (Deines and Gold, 1973; Javoy et al., 1986). Carbonatites also occur in association with many LIPs - perhaps due to low-degree melting beneath or within thick continental lithosphere - though their relationship with the petrogenesis and emplacement of the basaltic lavas remains uncertain (e.g. Bell and Tilton, 2002; Black and Gibson, 2019; Gibson et al., 2006). Perhaps most importantly, unlike in silicate melts, the majority of carbon in carbonatites crystallizes as carbonate minerals rather than degassing, reducing susceptibility to carbon isotope fractionation due to degassing. However, a major challenge to interpreting data from carbonatites is their susceptibility to alteration. Alkali carbonatites from Tanzania exposed to weathering for only a few weeks can show marked shifts to higher $\delta^{18}\text{O}$, with accompanying changes in $\delta^{13}\text{C}$ (Keller and Hoefs, 1995).

Here we assemble carbon and oxygen isotope data from carbonatites to infer the carbon isotope composition of the magmas of three different LIPs. Both Deccan Traps and Siberian

Traps magmatism overlapped in time with major mass extinctions (the 66 Ma end-Cretaceous mass extinction and the 252 Ma end-Permian mass extinction, respectively), though the relative importance of the Chicxulub impact and Deccan volcanism for the end-Cretaceous mass extinction remains the subject of debate (e.g. Henehan et al., 2019; Schoene et al., 2019; Sprain et al., 2019). Siberian Traps magmatism also coincided with a large negative carbon isotope excursion (Burgess and Bowring, 2015). While Paraná-Etendeka magmatism did not coincide with a mass extinction, it has been linked with the Valanginian oceanic anoxic event and associated positive carbon isotope excursion (Erba et al., 2004). We use carbonatite $\delta^{13}\text{C}$ systematics from these provinces to assess the carbon isotope composition of LIP magmas and to constrain the roles of mantle and lithospheric carbon reservoirs in surface carbon cycle disruption.

2. Geologic Setting

2.1 Large Igneous Provinces

LIPs are voluminous provinces consisting mainly of thick successions of flood basalts emplaced during individual eruptive episodes over $\sim 10^5$ - 10^6 years. They occur in intraplate settings and can encompass several million cubic kilometers of lava and associated intrusive bodies (Courtillet and Renne, 2003). LIPs are widely regarded to be the product of the upwelling of deep-sourced mantle plumes (White and McKenzie, 1995). Melt is produced during decompression and rifting when a high-temperature plume impinges on the base of the

lithosphere. Carbon released by a continental LIP can originate in three main reservoirs (Black and Gibson, 2019):

- The convecting mantle: Carbon dioxide in the convecting mantle is highly incompatible and partitions almost entirely into the melt phase.
- The subcontinental lithospheric mantle: This is thought to be a vast store for carbon that has accumulated and been enriched by infiltration of carbon-rich melts. Remobilization of this stored carbon may be triggered by the passage of a mantle plume (Foley and Fischer, 2017).
- Crustal rocks: Sedimentary rocks, such as carbonates and evaporites, are significant sources of carbon. Depending on the country rock lithology, the amount of carbon degassed by contact metamorphism during LIP emplacement may be more voluminous than that degassed from the magma (Ganino and Arndt, 2009).

Major perturbations of the carbon cycle are often coincident with LIPs. Strong global warming, spikes in atmospheric $p\text{CO}_2$, ocean acidification, and negative carbon isotope excursions occurring at the time of LIP volcanism are the strongest lines of evidence for a link to climate change (though not all are associated with every LIP) (Black and Gibson, 2019).

2.2 Carbon isotope excursions

The isotopes of carbon have the same number of protons but different numbers of neutrons, resulting in different atomic weights. Of the three naturally occurring carbon isotopes, ^{12}C and ^{13}C are stable, while ^{14}C is a radioactive isotope that decays to ^{14}N (and is used in the radiometric dating of biological material). The ratio of “heavy” ^{13}C to “light” ^{12}C in a given

substance is reported relative to a standard reference, by convention, the Vienna Pee Dee Belemnite (VPDB) – originally a fossilized shell collected from South Carolina. Carbon isotope ratios are expressed using the delta (δ) notation in parts per thousand and derived from the following equation:

$$\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{reference}}}{(^{13}\text{C}/^{12}\text{C})_{\text{reference}}}$$

Differences in the isotope ratio of various substances is the result of fractionation, a process that partitions isotopes between two interacting pools of carbon. For example, a plant producing organic matter will preferentially use the lighter ^{12}C isotopes it gathers from the atmosphere, (negligibly) enriching the atmosphere in ^{13}C and creating matter with a relatively light (^{13}C depleted) carbon isotope composition.

On geologic timescales, the ocean and atmosphere behave as a single carbon reservoir because of the continuous contact and exchange between them. When there is a change in the flux of carbon into the atmosphere (e.g. increased volcanic outgassing), that change will propagate through the oceanic dissolved inorganic carbon (DIC) pool. Changes in the carbon isotope composition of the ocean are recorded in the carbonate and organic matter of marine sediments. The carbon isotope record is generally stable, but high-amplitude excursions occur (up to 8‰), particularly during major extinction intervals and LIP magmatism (Schobben et al., 2019). Negative isotope excursions are thought to correspond to a large influx of isotopically light carbon (Black and Gibson, 2019).

2.3 The Guli massif (Siberian Traps), the Deccan Traps, and Paraná-Etendeka Traps

The carbonatite-bearing Guli complex is among the largest alkaline-ultramafic intrusive complexes in the world (Egorov, 1970; Yegorov, 1989), although it represents a tiny fraction of the volume of the Siberian Traps (Figure 1A), which emplaced an estimated $7\text{--}15 \times 10^6 \text{ km}^3$ magma as intrusions in the lithosphere and as extrusive lavas (Saunders, 2016). The main phase of Siberian Traps magmatism spanned $< 1 \text{ Myr}$, with the oldest volcanic rocks dated at $252.27 \pm 0.011 \text{ Ma}$ (Burgess and Bowring, 2015). Baddeleyite in the Guli carbonatites has been dated at $250.2 \pm 0.3 \text{ Ma}$ (Figure 2; Kamo et al., 2003), marking the youngest dated Siberian Traps rocks in the region, though direct comparison of this age with those in Burgess and Bowring, (2015) requires caution because the former predates the EARTHTIME initiative (Condon et al., 2015). The Guli is exposed across an area spanning approximately $40 \times 50 \text{ km}$ (Figure 1B). Along with the Odikhincha, Kugda, and Bor-Kuryakh massifs, it is one of several alkaline-ultramafic intrusions within the broader Maymecha-Kotuy province of the Siberian Traps (Kogarko and Zartman, 2006; Vasil'Ev and Gora, 2012). These intrusions are thought to represent the final stages of Siberian magmatism. These carbonatites crosscut dunite, pyroxenite, and alkaline rocks within the crescent-shaped Guli pluton (Kogarko and Zartman, 2006; Yegorov, 1989). The petrogenesis of the Guli and other Siberian ultramafic massifs is enigmatic. Early workers proposed the Guli complex was emplaced in a sequence of intruding phases (Egorov, 1970; Epshteyn and Anikeyeva, 1965), consisting of dunites, alkaline ultramafic rocks, nephelinitic basaltic rocks, alkaline syenites, and carbonatites. Fedorenko and Czamanske (1997) argued that the Guli encompasses both intrusive and extrusive rocks. Proposed mechanisms for magma genesis include fractionation from LIP magma bodies (Simonov et al., 2016) or diapiric emplacement from mantle depths, possibly driven by the buoyancy of volatile-rich components (Burg et al., 2009; Lazarenkov and Landa, 1992).

The Deccan Traps large igneous province, located in western India, currently occupies 500,000 km³ and had an original eruptive volume of approximately 1.3×10^6 km³ (Jay and Widdowson, 2008). The main phase of the eruptions lasted over 750,000 years, predating the Cretaceous-Paleogene boundary (ca. 66 Mya) by 250,000 years (Schoene et al., 2015). The end-Cretaceous mass extinction was one of the largest and is famous for wiping out all nonavian dinosaurs. The Deccan Traps also temporally overlap the Chicxulub crater in the Yucatan Peninsula of Mexico, which has been proposed as the mechanism for the mass extinction at this transition (e.g. Schulte et al., 2010), however, there is evidence for ecological deterioration preceding the impact event (e.g. Wilson, 2014). The end-Cretaceous mass extinction is marked by negative carbon isotope excursions of 1-2‰ (e.g. Punekar et al., 2016). As in the Siberian Traps, carbonatite complexes in the Deccan Traps (and Paraná-Etendeka Traps) commonly occur in association with alkaline magmas such as lamprophyres, nephelinites, or syenites (e.g. Le Roex and Lanyon, 1998 and Ray and Ramesh, 1999a). Well-documented carbonatite complexes include the Amba Dongar, Mundwara, and Sarnu-Dandali provinces (e.g. Ray and Ramesh, 1999a; Simonetti et al., 1995; Srivastava, 1997; Viladkar and Schidlowski, 2000). The origin of these complexes has been linked with nearby rift systems (e.g. Ray and Ramesh, 1999a). While available geochronology is uncertain, emplacement of Deccan carbonatites is thought to both precede and follow the main stage of the Deccan volcanism (Ernst and Bell, 2010).

Gibson et al. (2006) found a similar age distribution of alkaline magmatism within the ~135 Ma Paraná-Etendeka Traps in South America and southwest Africa. They comprise a large igneous province with an original volume in excess of 2.3×10^6 km³ (Courtillet and Renne, 2003). A substantial amount of this volume erupted approximately 135-134 Mya (Baksi, 2018), predating the Jurassic-Cretaceous boundary by ~10 Mya. It is the only major LIP that has not

been correlated with a mass extinction (Courtillet and Renne, 2003), but the increase in atmospheric CO₂ caused by the emplacement of the Paraná-Etendeka Traps may have been responsible for the Valanginian event: a global perturbation of the carbon cycle marked by an oceanic anoxic event and a positive isotope excursion of ~2‰ (e.g. Erba et al., 2004).

3. Methods

Samples from the Guli alkaline ultramafic massif (Figures 3 and 4) were collected during field work in the summer of 2008. Two subsamples were taken from each Guli carbonatite to test for heterogeneity due to alteration. Sample chips were pulverized in a shatterbox. Carbon and oxygen isotope compositions were determined using the H₃PO₄ digestion method in a Kiel IV Carbonate Device. ¹⁸O/¹⁶O and ¹³C/¹²C ratios were measured against a NBS19 standard, using a Delta V plus mass spectrometer at the Lamont-Doherty Earth Observatory in New York. Each subsample was analyzed two to four times to assess reproducibility and heterogeneity. δ¹⁸O values recorded relative to VPBD were converted to values relative to SMOW (standard mean ocean water) and will be reported this way henceforth. Major and trace element data were also collected at Activation Laboratories for 14 Guli carbonatite samples using inductively coupled plasma optical emission spectrometry for major elements and fusion inductively coupled plasma mass spectrometry for trace elements. Total FeO was determined by titration. Carbon and sulfur were measured with an induction furnace coupled to infrared sensors.

261 additional LIP carbonatite carbon and oxygen isotope ratios from the Deccan Traps and Paraná-Etendeka were compiled from the Geochemistry of Rocks of the Oceans and Continents (GEOROC) database (Table 1). Carbonatites from each of these provinces have been

the subject of detailed study (Alberti et al., 1999; Comin-Chiaramonti et al., 2002; Haynes et al., 2002; Le Roex and Lanyon, 1998; Morikiyo et al., 1990; Ray and Ramesh, 1999a; Ruberti et al., 2002; Santos and Clayton, 1995; Simonetti et al., 1995; Srivastava, 1997; Toyoda et al., 1994; Viladkar and Schidlowski, 2000). We also compare the data from carbonatites with data from a global database of diamond $\delta^{13}\text{C}$ compiled by Cartigny et al. (2014), and canonical mantle values (Bindeman, 2008; Pineau and Javoy, 1983) (Figure 5).

To track carbon isotope evolution in a hypothetical open-system LIP magma chamber undergoing simultaneous recharge and crystallization with periodic eruptions, we adapted an existing geochemical model (Lee et al., 2014). For a given magma chamber and recharge composition, the model tracks changes in melt composition based on partitioning between melt, fractionating crystal assemblage, and an exsolved volatile phase (Lee et al., 2014). Eruptions take place for a given mass change ΔM_{ch} relative to the initial chamber mass (in this case we assume a critical mass change of 10% for eruption, but the results are not strongly sensitive to this assumption). Carbon isotope evolution of the melt and exsolved phase at each model step is calculated with a mass-balance approach. The $\delta^{13}\text{C}_{\text{melt}}$ and $\delta^{13}\text{C}_{\text{fluid}}$ are related by a fluid-melt fractionation factor, $\Delta_{\text{fluid-melt}}$, here assumed to be $\sim 4.25\text{‰}$ (Gerlach and Taylor, 1990; Javoy et al., 1978), which implies that melt is in equilibrium with fluids or vapors with $\delta^{13}\text{C}$ about 4‰ heavier than that of the melt. At each step n , we calculate changes in $\delta^{13}\text{C}$ due to magma mixing and degassing separately. Assuming recharge mass of dM_{re} with carbon isotope composition $\delta^{13}\text{C}_{\text{re}} = -5$ and carbon concentration C_{re} , the carbon isotope ratios of the replenished but not degassed melt is the mass-weighted average of the $\delta^{13}\text{C}$ of recharge and the $\delta^{13}\text{C}$ of the carbon dissolved in the magma in the magma chamber from the preceding step,

$$\delta^{13}\text{C}_{\text{melt},n-1} M_{\text{ch},n-1} C_{\text{ch}}:$$

$$\delta^{13}\text{C}_{\text{melt,undegassed}} = \frac{\delta^{13}\text{C}_{\text{melt},n-1}M_{\text{ch},n-1}C_{\text{ch}} + \delta^{13}\text{C}_{\text{re}}dM_{\text{re}}C_{\text{re}}}{M_{\text{ch},n-1}C_{\text{ch}} + dM_{\text{re}}C_{\text{re}}}.$$

After fractional crystallization (where carbon is taken to be perfectly incompatible and thus becomes supersaturated in the melt), we assume that all carbon in excess of a specified solubility C_{ch} exsolves ($dM_{\text{carb,ex}}$), and calculate post-degassing $\delta^{13}\text{C}$:

$$\delta^{13}\text{C}_{\text{melt}} = \frac{\delta^{13}\text{C}_{\text{melt,undegassed}}(M_{\text{ch}}C_{\text{ch}} + dM_{\text{carb,ex}}) - \delta^{13}\text{C}_{\text{fluid}}dM_{\text{carb,ex}}}{M_{\text{ch}}C_{\text{ch}}}$$

obtained from rearranging the carbon isotope mass balance equation for degassed melt, fluid, and the undegassed melt.

4. Results

Available $\delta^{13}\text{C}$ values from LIP carbonatites ranges from -12.2 to +4.8‰. As shown in Figure 5, the distribution of LIP carbonatite $\delta^{13}\text{C}$ values lacks the ‘negative tail’ observed in $\delta^{13}\text{C}$ measured in diamonds (e.g. Cartigny et al., 2014). LIP carbonatites closely fit canonical mantle $\delta^{13}\text{C}$ values, with the majority plotting within the depleted mantle range (-8 to -4‰) and very few lighter than -8.50‰. Guli carbonatites had a mean $\delta^{13}\text{C}$ of $-3.37 \pm 0.98\text{‰}$; and a mean $\delta^{18}\text{O}$ of $+10.12 \pm 3.38\text{‰}$. This compares to a mean $\delta^{13}\text{C}$ of $-4.40 \pm 2.06\text{‰}$; and a mean $\delta^{18}\text{O}$ of $+12.34 \pm 5.14\text{‰}$ for all available carbonatites from LIPs. We performed a one-way ANOVA and Tukey-Kramer post hoc test, despite the heterogeneity of variance and non-normal distribution of our data, and found that there was a statistically significant difference between the Paraná-Etendeka mean $\delta^{13}\text{C}$ and those of the other two LIPs ($p = 0.05$; Figure 6). We also performed a Welch’s ANOVA and Games-Howell test which indicated that the mean $\delta^{13}\text{C}$ of all

three groups are statistically significantly different ($p = 0.05$). Both these post hoc test results must be considered with the caveat that all Siberian Traps data comes from a single site.

Guli $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ show a moderate positive correlation ($R=0.66$). Deccan and Paraná-Etendeka data have a weak positive correlation ($R=0.23$ and $R=0.29$ respectively), possibly due to the variability of many sites sampled across each province. $\delta^{18}\text{O}$ data from all three LIPs span a range of values much broader than their $\delta^{13}\text{C}$ ranges. The oxygen isotope composition of Earth's mantle is $\delta^{18}\text{O} = +5.5 \text{ ‰}$ (e.g. Matthey et al., 1994). The primary igneous carbonatite oxygen isotope range may reach more positive values than this due to fractionation during low degree melting (Eiler, 2001), yielding $\delta^{18}\text{O} \approx 5.5\text{-}8.5 \text{ ‰}$ (Keller and Hoefs, 1995).

Rare earth elements (REEs) are typically strongly enriched in carbonatites. This enrichment has been attributed to very small degrees of partial melting (e.g Bell and Tilton, 2002; Gibson et al., 2006) or enrichment during carbonatite-silicate liquid immiscibility (e.g. Weidendorfer et al., 2017). REE concentrations from the Guli carbonatites range across an order of magnitude (Figure 7A). The Guli massif includes two main carbonatite complexes (Figures 1 and 4). Carbonatites from the southern complex (Figure 7B) show steep, near-linear REE enrichment patterns typical of carbonatites, and a decrease in overall REE concentration with increasing $\delta^{18}\text{O}$. Those from the northern complex (Figure 7C) produce profiles that drop steeply through the lighter REEs and plateau towards the heavy REEs. Principle Component Analysis (PCA) of the Guli REE profiles determined two components explained 99% of the variance. The first accounted for 94.6%, with heavy loadings (> 0.4) on La, Ce, and Pr. The second accounted for 4.9% of variance with heavy loading on La (0.81).

5. Discussion

5.1 The fidelity of carbonatites and their relationship with other LIP magmas

The relationship between carbonatite $\delta^{13}\text{C}$ data and the broader story of LIP carbon depends on the reliability of carbonatites as carbon isotope records and on the relationship between the petrogenesis of carbonatites and that of other LIP magmas.

Carbonatites are susceptible to alteration. Nevertheless, several lines of evidence suggest our carbon isotope data are generally robust. $\delta^{18}\text{O}$ values do not reflect equilibration with light $\delta^{18}\text{O}$ from meteoritic water (e.g. Harrison, 2009). We split each of our Guli carbonatite samples into at least two subsamples. Replicate analyses of these subsamples revealed highly reproducible $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, implying that heterogeneity resulting from local diagenesis is negligible. Finally, clumped isotope thermometry of carbonatites suggests that open system exchange of carbon and oxygen atoms is inefficient at temperatures below 100-300 °C (Dennis and Schrag, 2010), permitting the preservation of isotope signatures on timescales of 10^8 years.

Whether or not the $\delta^{13}\text{C}$ of carbonatites associated with LIPs is representative of the isotopic composition of tholeiitic flood basalt magmas depends on the organization of LIP plumbing systems and the petrogenesis of carbonatites. As discussed above, the petrogenesis of Guli and other Siberian alkaline-ultramafic intrusions, including associated carbonatites, remains an open question. In general, LIP carbonatites are thought to originate through a multi-stage process involving very low-degree melting followed by liquid immiscibility in a carbonated silicate melt and finally crystallization in the resulting carbonatite magma (e.g. Bell and Tilton, 2002; Gibson et al., 2006; Ray et al., 2000; Weidendorfer et al., 2017). If low-degree melting takes place on the margins of an impinging plume head, or if carbon in low-degree melts

exchanges with the higher-degree melts that are parental to tholeiitic magmas, carbonatites may be representative of LIP carbon in a broad sense. On the other hand, if carbonatites originate through low degree melting of the mantle lithosphere (e.g. Gibson et al., 2006), they may be isolated from the main LIP plumbing system. In this case they could only reveal information about carbon from the mantle lithosphere. This latter possibility would nevertheless be important owing to the status of the subcontinental mantle lithosphere as a major potential reservoir of carbon that could be tapped during LIP magmatism (e.g. Black and Gibson, 2019; Foley and Fischer, 2017).

5.2 The evolution of carbon in the mantle lithosphere on geologic timescales

Estimates of the carbon content of the subcontinental mantle lithosphere (SCLM) range from average concentration of <700 ppm C to several weight percent in the lowermost SCLM (Foley and Fischer, 2017; Lee et al., 2019), which is one to four orders of magnitude higher than the C contents of the convecting mantle (Dasgupta and Hirschmann, 2010; Tucker et al., 2019). SCLM carbon is thought to accumulate on billion-year timescales through fluxing and freezing of metasomatic fluids. Mantle plumes have been hypothesized to be a major source of the fluids that build the SCLM reservoir (Foley, 2008; Foley and Fischer, 2017). Guex et al. (2016) also proposed that LIP magmatism serves as a mechanism for disruption of the SCLM and release of SCLM volatiles.

The carbon isotope composition of a hypothesized SCLM carbon reservoir remains an important open question. To investigate the expected carbon isotope composition of the fluids contributed during plume-related melting, we employ a magma chamber model (Lee et al., 2014) that has been adapted to track magmatic and exsolved carbon isotopes in continuously

recharging, erupting, and crystallizing magma chambers. This scenario is based on the expectation that deep LIP magma chambers are long-lived, open-system reservoirs (e.g. Black and Manga, 2017; Cox, 1980; Heinonen et al., 2019). Our geochemical model shows that in this scenario the $\delta^{13}\text{C}$ of exsolved fluids and vapors is several per mil heavier than that of the parental melt, consistent with the distribution of LIP carbonatite $\delta^{13}\text{C}$ presented here. We calculate that the $\delta^{13}\text{C}$ of fluids exsolved from a carbon-saturated open-system magma chamber range from -1 to -5 ‰ for a primary melt $\delta^{13}\text{C} = -5$ (Figure 8). This range represents the $\delta^{13}\text{C}$ ratio of fluids available to flux the mantle lithosphere. Consequently, if SCLM carbon derives from partial degassing of mantle melts, it would tend to be slightly isotopically heavier than the mantle source. Similarly, partially degassed basaltic magmas that freeze as eclogites at Moho depths would be expected to retain fractionated, slightly light $\delta^{13}\text{C}$ ratios relative to the mantle source (Figure 8).

The distribution of LIP carbonatite $\delta^{13}\text{C}$ ratios extends to -1 ‰ for the Siberian Traps and +1 ‰ for the Deccan Traps and Parana-Etendeka (excluding a single outlier). The presence of carbonatites with $\delta^{13}\text{C}$ ratios more positive than MORB has been reported previously, and has been attributed to fractionation of calcite from a carbonatite melt in equilibrium with CO_2 and H_2O fluids (Ray and Ramesh, 1999b). If carbonatites derive from melting of the mantle lithosphere, this distribution is also consistent with the presence of a component of SCLM carbon that is slightly heavier isotopically than the depleted mantle. Alternatively, if LIP carbonatites originate through fractionation in LIP-scale magma chambers, they may represent direct samples of the metasomatic fluids that flux the lithosphere during LIP activity. In either case, our modeling and carbonatite $\delta^{13}\text{C}$ ratios raise the possibility of a SCLM carbon reservoir that is slightly (several ‰) heavier than that of the convecting upper mantle. This hypothesis is

in agreement with observed slightly heavier $\delta^{13}\text{C}$ ratios from the East African Rift (Fischer et al., 2009)

5.3 Carbonatite outgassing and broader implications of LIP outgassing for carbon isotope excursions

Paraná-Etendeka carbonatites carry mean $\delta^{13}\text{C}$ that is subtly but significantly (see Section 4 above) lighter than Deccan and Siberian carbonatites. One possible reason for this province-to-province difference in $\delta^{13}\text{C}$ relates to the heterogeneities in the mantle lithosphere underlying each LIP. In Section 5.2, we suggested that through time the SCLM may develop slightly heavier $\delta^{13}\text{C}$ than that of the convecting mantle. The lithospheric mantle beneath the Paraná-Etendeka LIP is Proterozoic to Cenozoic in age, in contrast with the Archean lithosphere beneath the Siberian Traps and Deccan Traps (Guex et al., 2016).

Ray and Pande, (1999) suggested that rapid release of CO_2 from Deccan carbonatites and associated alkaline rocks could have played a role in the end-Cretaceous mass extinction. Both the timing and the size of the Guli complex suggest that in itself it did not play a major role in end-Permian carbon cycle disruption. Based on the available U-Pb dates, emplacement of the Guli postdated the main end-Permian carbon isotope excursion by ~ 2 Myr (Figure 2). The exposed areas of the northern and southern Guli carbonatite stocks are $\sim 3 \text{ km}^2$ and $\sim 5 \text{ km}^2$ respectively (Yegorov, 1989). Assuming these stocks have similar vertical and horizontal extents implies a total volume of $\sim 10 \text{ km}^3$. Even allowing for the very high CO_2 contents of these magmas ($\sim 40\%$), 10% degassing yields a small fraction of the CO_2 available from the tholeiitic magmas. On the other hand, the volume of alkaline Siberian Traps rocks is larger by several orders of magnitude (e.g. Fedorenko and Czamanske, 1997), and the volume of these rocks may

be decoupled from their carbon degassing potential (e.g. Black and Gibson, 2019). The scale of carbon release from alkaline LIP magmas, and the relationship of alkaline magmatism with the overall evolution of LIPs, thus merits further investigation.

While they are not directly implicated in carbon cycle disruption, large igneous province carbonatites offer one of the few available constraints on the isotopic composition of carbon released by LIP magmas. If our carbonatite $\delta^{13}\text{C}$ data are representative of LIP magmas, there is only a small difference between magmatic carbon released by LIPs and the $\delta^{13}\text{C}$ of the oceanic carbon pool. Thus, while LIP magma does have some leverage to create an isotope excursion in the marine carbonate record, is too isotopically heavy to easily account for the negative carbon isotope excursions that coincide with LIPs including the Siberian Traps and the Central Atlantic Magmatic Province, as it would require a very large release of mantle carbon over a very short timescale (Cui et al., 2013; Payne and Kump, 2007). Instead, injection of light carbon from crustal or surface reservoirs (e.g. Ganino and Arndt, 2009), or shifts in the surface-to-deep ocean carbon isotope balance (e.g. Meyer et al., 2011), are the most plausible explanations for such excursions.

6. Conclusions

Constraints on the magnitude, tempo, and isotopic composition of carbon release are central to understanding the environmental and geochemical consequences of large igneous province magmatism (e.g. Black et al., 2018; Saunders, 2016). However, degassing obscures magmatic carbon systematics. While the $\delta^{13}\text{C}$ of the depleted upper mantle is well-established as $\delta^{13}\text{C} = -6 \pm 2$ (Deines, 2002; Javoy et al., 1986; Javoy and Pineau, 1991; Pineau and Javoy, 1983),

the $\delta^{13}\text{C}$ of LIP magmas has remained the subject of conjecture (e.g. Bachan and Payne, 2016; Paris et al., 2012; Sobolev et al., 2011). We combine new data from Siberian Traps carbonatites from the Guli Massif with literature data from carbonatite complexes associated with the Deccan and Paraná-Etendeka Traps. These LIP carbonatite data yield a mean $\delta^{13}\text{C} = -4.40 \pm 2.06\text{‰}$, squarely in line with canonical mantle values. Because this value is close to the bulk $\delta^{13}\text{C}$ of the ocean-atmosphere system, an exceptionally large and rapid release of mantle carbon would be required to significantly impact marine carbon isotope records.

We therefore infer that injection of mantle carbon to the ocean-atmosphere system during LIP emplacement is not a viable trigger for major carbon isotope excursions like those that marked the end-Permian, end-Triassic, and Paleocene-Eocene extinction events. By elimination, these isotope excursions likely resulted from shifts in marine carbon isotope gradients and burial of organic matter (e.g. Meyer et al., 2011) or liberation of light carbon from crustal organic material, coal, or clathrates (e.g. Gutjahr et al., 2017; Heimdal et al., 2018). Outgassing of mantle carbon by LIPs has been proposed as a major driver of coeval climate warming (e.g. Joachimski et al., 2012). Carbonatite records of $\delta^{13}\text{C}$ do not exclude this scenario. Rather, if mantle carbon was a primary driver of climate warming during events like the Siberian Traps, Central Atlantic Magmatic Province, and North Atlantic Igneous Province (Gutjahr et al., 2018), an additional light carbon source is required to explain coincident carbon isotope excursions.

References

- Alberti, A., Castorina, F., Censi, P., Comin-Chiaramonti, P., Gomes, C.B., 1999. Geochemical characteristics of Cretaceous carbonatites from Angola. *J. African Earth Sci.* 29, 735–759. [https://doi.org/10.1016/S0899-5362\(99\)00127-X](https://doi.org/10.1016/S0899-5362(99)00127-X)
- Bachan, A., Payne, J.L., 2016. Modelling the impact of pulsed CAMP volcanism on $p\text{CO}_2$ and $\delta^{13}\text{C}$ across the Triassic – Jurassic transition 153, 252–270. <https://doi.org/10.1017/S0016756815000126>
- Baksi, A.K., 2018. Paraná flood basalt volcanism primarily limited to ~ 1 Myr beginning at 135 Ma: New $^{40}\text{Ar}/^{39}\text{Ar}$ ages for rocks from Rio Grande do Sul, and critical evaluation of published radiometric data. *J. Volcanol. Geotherm. Res.* 355, 66–77. <https://doi.org/10.1016/j.jvolgeores.2017.02.016>
- Bell, K., Tilton, G.R., 2002. Probing the mantle: The story from carbonatites. *Eos (Washington, DC)*. 83. <https://doi.org/10.1029/2002EO000190>
- Bindeman, I., 2008. Oxygen Isotopes in Mantle and Crustal Magmas as Revealed by Single Crystal Analysis. *Rev. Mineral. Geochemistry* 69, 445–478. <https://doi.org/10.2138/rmg.2008.69.12>
- Black, B.A., Gibson, S.A., 2019. Deep Carbon and the Life Cycle of Large Igneous Provinces. *Elements* 15, 319–324. <https://doi.org/10.2138/gselements.15.5.319>
- Black, B.A., Manga, M., 2017. Volatiles and the tempo of flood basalt magmatism. *Earth Planet. Sci. Lett.* 458, 130–140. <https://doi.org/10.1016/j.epsl.2016.09.035>
- Black, B.A., Neely, R.R., Lamarque, J.-F., Elkins-Tanton, L.T., Kiehl, J.T., Shields, C.A., Mills, M.J., Bardeen, C., 2018. Systemic swings in end-Permian climate from Siberian Traps carbon and sulfur outgassing. *Nat. Geosci.* 11, 949–954. <https://doi.org/10.1038/s41561-018-0261-y>
- Burg, J.P., Bodinier, J.L., Gerya, T., Bedini, R.M., Boudier, F., Dautria, J.M., Prikhodko, V., Efimov, A., Pupier, E., Balanec, J.L., 2009. Translithospheric mantle diapirism: Geological evidence and numerical modelling of the Kondyor zoned ultramafic complex (Russian Far-East). *J. Petrol.* 50, 289–321. <https://doi.org/10.1093/petrology/egn083>
- Burgess, S.D., Bowring, S.A., 2015. High-precision geochronology confirms voluminous magmatism before, during, and after Earth's most severe extinction. *Sci. Adv.* 1. <https://doi.org/10.1126/sciadv.1500470>
- Cartigny, P., Palot, M., Thomassot, E., Harris, J.W., 2014. Diamond Formation: A Stable Isotope Perspective. *Annu. Rev. Earth Planet. Sci.* 42, 699–732. <https://doi.org/10.1146/annurev-earth-042711-105259>
- Comin-Chiaramonti, P., Gomes, C.B., Castorina, F., Censi, P., Antonini, P., Furtado, S., Ruberti, E., Scheibe, L.F., 2002. Geochemistry and Geodynamic Implications of the Anitápolis and Lages Alkaline-Carbonatite Complexes, Santa Catarina State, Brazil. *Rev. Bras. Geociências* 32, 16.
- Condon, D.J., Schoene, B., McLean, N.M., Bowring, S.A., Parrish, R.R., 2015. ScienceDirect Metrology and traceability of U-Pb isotope dilution geochronology (EARTHTIME Tracer Calibration Part I). *Geochim. Cosmochim. Acta* 164, 464–480. <https://doi.org/10.1016/j.gca.2015.05.026>
- Courtillot, V.E., Renne, P.R., 2003. On the ages of flood basalt events. *Comptes Rendus - Geosci.* 335, 113–140. [https://doi.org/10.1016/S1631-0713\(03\)00006-3](https://doi.org/10.1016/S1631-0713(03)00006-3)
- Cox, K.G., 1980. A model for flood basalt volcanism. *J. Petrol.* 21, 629–650.

- <https://doi.org/10.1093/petrology/21.4.629>
- Cui, Y., Kump, L.R., Ridgwell, A., 2013. Initial assessment of the carbon emission rate and climatic consequences during the end-Permian mass extinction. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 389, 128–136. <https://doi.org/10.1016/j.palaeo.2013.09.001>
- Dasgupta, R., Hirschmann, M.M., 2010. The deep carbon cycle and melting in Earth's interior. *Earth Planet. Sci. Lett.* 298, 1–13. <https://doi.org/10.1016/j.epsl.2010.06.039>
- Deines, P., 2002. The carbon isotope geochemistry of mantle xenoliths. *Earth-Science Rev.* 58, 247–278. [https://doi.org/10.1016/S0012-8252\(02\)00064-8](https://doi.org/10.1016/S0012-8252(02)00064-8)
- Deines, P., Gold, D.P., 1973. The isotopic composition of carbonatite and kimberlite carbonates and their bearing on the isotopic composition of deep-seated carbon. *Geochim. Cosmochim. Acta* 37, 1709–1733. [https://doi.org/10.1016/0016-7037\(73\)90158-0](https://doi.org/10.1016/0016-7037(73)90158-0)
- Dennis, K.J., Schrag, D.P., 2010. Clumped isotope thermometry of carbonatites as an indicator of diagenetic alteration. *Geochim. Cosmochim. Acta* 74, 4110–4122. <https://doi.org/10.1016/j.gca.2010.04.005>
- Egorov, L.S., 1970. Carbonatites and ultrabasic-alkaline rocks of the maimecha-kotui region, N. Siberia. *Lithos* 3, 341–359. [https://doi.org/10.1016/0024-4937\(70\)90041-1](https://doi.org/10.1016/0024-4937(70)90041-1)
- Eiler, J.M., 2001. Oxygen isotope variations of basaltic lavas and upper mantle rocks (in Stable isotope geochemistry). *Rev. Mineral. Geochemistry* 43, 319–364. <https://doi.org/10.2138/gsrmg.43.1.319>
- Epshteyn, Y.M., Anikeyeva, L.I., 1965. Problems in geology and petrology of ultrabasic alkalic intrusive rock complexes. *Int. Geol. Rev.* 7, 307–324. <https://doi.org/10.1080/00206816509474113>
- Erba, E., Bartolini, A., Larson, R.L., 2004. Valanginian Weissert oceanic anoxic event. *Geology* 32, 149–152. <https://doi.org/10.1130/G20008.1>
- Ernst, R.E., Bell, K., 2010. Large igneous provinces (LIPs) and carbonatites. *Mineral. Petrol.* 98, 55–76. <https://doi.org/10.1007/s00710-009-0074-1>
- Fedorenko, V., Czamanske, G., 1997. Results of new field and geochemical studies of the volcanic and intrusive rocks of the maymecha-kotuy area, siberian flood-basalt province, russia. *Int. Geol. Rev.* 39, 479–531. <https://doi.org/10.1080/00206819709465286>
- Fischer, T.P., Burnard, P., Marty, B., Hilton, D.R., Füre, E., Palhol, F., Sharp, Z.D., Mangasini, F., 2009. Upper-mantle volatile chemistry at Oldoinyo Lengai volcano and the origin of carbonatites 459, 77–80. <https://doi.org/10.1038/nature07977>
- Foley, S.F., 2008. Rejuvenation and erosion of the cratonic lithosphere. *Nat. Geosci.* 1, 503–510. <https://doi.org/10.1038/ngeo261>
- Foley, S.F., Fischer, T.P., 2017. An essential role for continental rifts and lithosphere in the deep carbon cycle. *Nat. Geosci.* 10, 897–902. <https://doi.org/10.1038/s41561-017-0002-7>
- Ganino, C., Arndt, N.T., 2009. Climate changes caused by degassing of sediments during the emplacement of large igneous provinces. *Geology* 37, 323–326. <https://doi.org/10.1130/G25325A.1>
- Gerlach, T.M., Taylor, B.E., 1990. Carbon isotope constraints on degassing of carbon dioxide from Kilauea Volcano. *Geochim. Cosmochim. Acta* 54, 2051–2058. [https://doi.org/10.1016/0016-7037\(90\)90270-U](https://doi.org/10.1016/0016-7037(90)90270-U)
- Gibson, S.A., Thompson, R.N., Day, J.A., 2006. Timescales and mechanisms of plume-lithosphere interactions: $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology and geochemistry of alkaline igneous rocks from the Paraná-Etendeka large igneous province. *Earth Planet. Sci. Lett.* 251, 1–17. <https://doi.org/10.1016/j.epsl.2006.08.004>

- Guex, J., Pilet, S., Müntener, O., Bartolini, A., Spangenberg, J., Schoene, B., Sell, B., Schaltegger, U., 2016. Thermal erosion of cratonic lithosphere as a potential trigger for mass-extinction. *Sci. Rep.* 6, 1–9. <https://doi.org/10.1038/srep23168>
- Gutjahr, M., Ridgwell, A., Sexton, P.F., Anagnostou, E., Pearson, P.N., Pälke, H., Norris, R.D., Thomas, E., Foster, G.L., 2017. Very large release of mostly volcanic carbon during the Palaeocene–Eocene Thermal Maximum. *Nature* 548, 573–577. <https://doi.org/10.1038/nature23646>
- Harrison, T.M., 2009. The Hadean Crust: Evidence from >4 Ga Zircons. *Annu. Rev. Earth Planet. Sci.* 37, 479–505. <https://doi.org/10.1146/annurev.earth.031208.100151>
- Haynes, E.A., Moecher, D.P., Spicuzza, M.J., 2002. Oxygen isotope composition of carbonates, silicates, and oxides in selected carbonatites: Constraints on crystallization temperatures of carbonatite magmas. *Chem. Geol.* 193, 43–57. [https://doi.org/10.1016/S0009-2541\(02\)00244-9](https://doi.org/10.1016/S0009-2541(02)00244-9)
- Heimdal, T.H., Svensen, H.H., Ramezani, J., Iyer, K., Pereira, E., Rodrigues, R., Jones, M.T., Callegaro, S., 2018. Large-scale sill emplacement in Brazil as a trigger for the end-Triassic crisis. *Sci. Rep.* 8, 1–12. <https://doi.org/10.1038/s41598-017-18629-8>
- Heinonen, J.S., Luttinen, A. V., Spera, F.J., Bohrsen, W.A., 2019. Deep open storage and shallow closed transport system for a continental flood basalt sequence revealed with Magma Chamber Simulator. *Contrib. to Mineral. Petrol.* 174. <https://doi.org/10.1007/s00410-019-1624-0>
- Henehan, M.J., Ridgwell, A., Thomas, E., Zhang, S., Alegret, L., Schmidt, D.N., Rae, J.W.B., Witts, J.D., Landman, N.H., Greene, S.E., Huber, B.T., Super, J.R., Planavsky, N.J., Hull, P.M., 2019. Rapid ocean acidification and protracted Earth system recovery followed the end-Cretaceous Chicxulub impact. *Proc. Natl. Acad. Sci.* 1–5. <https://doi.org/10.1073/pnas.1905989116>
- Javoy, M., Pineau, F., 1991. The volatiles record of a “popping” rock from the Mid-Atlantic Ridge at 14°N: chemical and isotopic composition of gas trapped in the vesicles. *Earth Planet. Sci. Lett.* 107, 598–611. [https://doi.org/10.1016/0012-821X\(91\)90104-P](https://doi.org/10.1016/0012-821X(91)90104-P)
- Javoy, M., Pineau, F., Delorme, H., 1986. Carbon and nitrogen isotopes in the mantle. *Chem. Geol.* 57, 41–62. [https://doi.org/10.1016/0009-2541\(86\)90093-8](https://doi.org/10.1016/0009-2541(86)90093-8)
- Javoy, M., Pineau, F., Iiyama, I., 1978. Experimental determination of the isotopic fractionation between gaseous CO₂ and carbon dissolved in tholeiitic magma - A preliminary study. *Contrib. to Mineral. Petrol.* 67, 35–39. <https://doi.org/10.1007/BF00371631>
- Jay, A.E., Widdowson, M., 2008. Stratigraphy, structure and volcanology of the SE Deccan continental flood basalt province: Implications for eruptive extent and volumes. *J. Geol. Soc. London.* 165, 177–188. <https://doi.org/10.1144/0016-76492006-062>
- Joachimski, M.M., Lai, X., Shen, S., Jiang, H., Luo, G., Chen, B., Chen, J., Sun, Y., 2012. Climate warming in the latest Permian and the Permian-Triassic mass extinction. *Geology* 40, 195–198. <https://doi.org/10.1130/G32707.1>
- Kamo, S.L., Czamanske, G.K., Amelin, Y., Fedorenko, V.A., Davis, D.W., Trofimov, V.R., 2003. Rapid eruption of Siberian flood-volcanic rocks and evidence for coincidence with the Permian-Triassic boundary and mass extinction at 251 Ma. *Earth Planet. Sci. Lett.* 214, 75–91. [https://doi.org/10.1016/S0012-821X\(03\)00347-9](https://doi.org/10.1016/S0012-821X(03)00347-9)
- Karlstrom, L., Richards, M., 2011. On the evolution of large ultramafic magma chambers and timescales for flood basalt eruptions. *J. Geophys. Res. Solid Earth* 116, 1–13. <https://doi.org/10.1029/2010JB008159>

- Keller, J., Hoefs, J., 1995. Stable Isotope Characteristics of Recent Natrocarbonatites from Oldoinyo Lengai, in: Carbonatite Volcanism: Oldoinyo Lengai and the Petrogenesis of Natrocarbonatites. pp. 113–123. https://doi.org/10.1007/978-3-642-79182-6_9
- Kogarko, L.N., Zartman, R.E., 2006. A Pb isotope investigation of the Guli massif, Maymecha-Kotuy alkaline-ultramafic complex, Siberian flood basalt province, Polar Siberia. *Mineral. Petrol.* 89, 113–132. <https://doi.org/10.1007/s00710-006-0139-3>
- Lazarenkov, V.G., Landa, E.A., 1992. Evidence of solid-state emplacement of the Konder Pluton and the problem of mantle diapirism. *Int. Geol. Rev.* 34, 617–628. <https://doi.org/10.1080/00206819209465626>
- Le Roex, A.P., Lanyon, R., 1998. Isotope and trace element geochemistry of Cretaceous Damaraland lamprophyres and carbonatites, northwestern Namibia: evidence for plume-lithosphere interactions. *J. Petrol.* 39, 1117–1146. <https://doi.org/10.1093/petroj/39.6.1117>
- Lee, C.-T.A., Jiang, H., Dasgupta, R., Torres, M., 2019. A Framework for Understanding Whole-Earth Carbon Cycling, *Deep Carbon: Past to Present*. Cambridge University Press. <https://doi.org/10.1017/9781108677950.011>
- Lee, C.T.A., Lee, T.C., Wu, C.T., 2014. Modeling the compositional evolution of recharging, evacuating, and fractionating (REFC) magma chambers: Implications for differentiation of arc magmas. *Geochim. Cosmochim. Acta* 143, 8–22. <https://doi.org/10.1016/j.gca.2013.08.009>
- Malich, N.S., Mironyuk, E.P., Tuganova, E.V., 1974. Geological map of Siberian platform and adjoining areas. Ministry of Natural Resources of the Russian Federation.
- Mattey, D., Lowry, D., Macpherson, C., 1994. Oxygen isotope composition of mantle peridotite. *Earth Planet. Sci. Lett.* 128, 231–241. [https://doi.org/10.1016/0012-821X\(94\)90147-3](https://doi.org/10.1016/0012-821X(94)90147-3)
- McDonough, W.F., Sun, S. -s., 1995. The composition of the Earth. *Chem. Geol.* 120, 223–253.
- Meyer, K.M., Yu, M., Jost, A.B., Kelley, B.M., Payne, J.L., 2011. $\delta^{13}\text{C}$ evidence that high primary productivity delayed recovery from end-Permian mass extinction. *Earth Planet. Sci. Lett.* 302, 378–384. <https://doi.org/10.1016/j.epsl.2010.12.033>
- Morikiyo, T., Hirano, H., Matsuhisa, Y., 1990. Carbon and oxygen isotopic composition of the carbonates from the Jacupiranga and Catalao I carbonatite complexes, Brazil. *Bull. Geol. Surv. Japan* 41, 8.
- Paris, G., Donnadiou, Y., Beaumont, V., Fluteau, F., Goddris, Y., 2012. Modeling the consequences on late Triassic environment of intense pulse-like degassing during the Central Atlantic Magmatic Province using the GEOCLIM model. *Clim. Past Discuss.* 8, 2075–2110. <https://doi.org/10.5194/cpd-8-2075-2012>
- Payne, J.L., Kump, L.R., 2007. Evidence for recurrent Early Triassic massive volcanism from quantitative interpretation of carbon isotope fluctuations 256, 264–277. <https://doi.org/10.1016/j.epsl.2007.01.034>
- Petersen, S. V., Dutton, A., Lohmann, K.C., 2016. End-Cretaceous extinction in Antarctica linked to both Deccan volcanism and meteorite impact via climate change. *Nat. Commun.* 7, 1–9. <https://doi.org/10.1038/ncomms12079>
- Pineau, F., Javoy, M., 1983. Carbon isotopes and concentrations in mid-ocean ridge basalts. *Earth Planet. Sci. Lett.* 62, 239–257. [https://doi.org/10.1016/0012-821X\(83\)90087-0](https://doi.org/10.1016/0012-821X(83)90087-0)
- Punekar, J., Keller, G., Khozyem, H.M., Adatte, T., Font, E., Spangenberg, J., 2016. A multi-proxy approach to decode the end-Cretaceous mass extinction. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 441, 116–136. <https://doi.org/10.1016/j.palaeo.2015.08.025>

- Ray, J.S., Pande, K., 1999. Carbonatite alkaline magmatism associated with continental flood basalts at stratigraphic boundaries: Cause for mass extinctions. *Geophys. Res. Lett.* 26, 1917–1920. <https://doi.org/10.1029/1999GL900390>
- Ray, J.S., Ramesh, R., 1999a. Evolution of carbonatite complexes of the Deccan flood basalt province: Stable carbon and oxygen isotopic constraints. *J. Geophys. Res. Solid Earth* 104, 29471–29483. <https://doi.org/10.1029/1999JB900262>
- Ray, J.S., Ramesh, R., 1999b. Rayleigh fractionation of stable isotopes from a multicomponent source. *Geochim. Cosmochim. Acta* 64, 299–306. [https://doi.org/10.1016/S0016-7037\(99\)00181-7](https://doi.org/10.1016/S0016-7037(99)00181-7)
- Ray, J.S., Ramesh, R., Pande, K., Trivedi, J.R., Shukla, P.N., Patel, P.P., 2000. Isotope and rare earth element chemistry of carbonatite-alkaline complexes of Deccan volcanic province: Implications to magmatic and alteration processes. *J. Asian Earth Sci.* 18, 177–194. [https://doi.org/10.1016/S1367-9120\(99\)00030-9](https://doi.org/10.1016/S1367-9120(99)00030-9)
- Ruberti, E., Castorina, F., Censi, P., Comin-Chiaramonti, P., Gomes, C.B., Antonini, P., Andrade, F.R.D., 2002. The geochemistry of the Barra do Itapirapuã carbonatite (Ponta Grossa Arch, Brazil): A multiple stockwork. *J. South Am. Earth Sci.* 15, 215–228. [https://doi.org/10.1016/S0895-9811\(02\)00031-7](https://doi.org/10.1016/S0895-9811(02)00031-7)
- Santos, R., Clayton, R.N., 1995. Variation of oxygen and carbon isotopes in carbonatites: A study of Brazilian alkaline complexes. *Geochim. Cosmochim. Acta* 59, 1339–1352.
- Saunders, A.D., 2016. 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. *Geol. Mag.* 153, 201–222. <https://doi.org/10.1017/S0016756815000175>
- Schobben, M., Schootbrugge, B. Van De, Wignall, P.B., 2019. Interpreting the Carbon Isotope Record of Mass Extinctions. *Elements* 15, 331–337. <https://doi.org/10.2138/gselements.15.5.331>
- Schoene, B., Eddy, M.P., Samperton, K.M., Keller, C.B., Keller, G., Adatte, T., Khadri, S.F.R., 2019. U-Pb constraints on pulsed eruption of the Deccan Traps across the end-Cretaceous mass extinction. *Science* (80-.). 363, 862–866. <https://doi.org/10.1126/science.aau2422>
- Schoene, B., Samperton, K.M., Eddy, M.P., Keller, G., Adatte, T., Bowring, S.A., Khadri, S.F.R., Gertsch, B., 2015. U-Pb geochronology of the Deccan Traps and relation to the end-Cretaceous mass extinction. *Science* (80-.). 347, 182–184. <https://doi.org/10.1126/science.aaa0118>
- Schulte, P., Alegret, L., Arenillas, I., Arz, J.A., Barton, P.J., Bown, P.R., Bralower, T.J., Christeson, G.L., Claeys, P., Cockell, C.S., Collins, G.S., Deutsch, A., Goldin, T.J., Goto, K., Grajales-Nishimura, J.M., Grieve, R.A.F., Gulick, S.P.S., Johnson, K.R., Kiessling, W., Koeberl, C., Kring, D.A., MacLeod, K.G., Matsui, T., Melosh, J., Montanari, A., Morgan, J. V., Neal, C.R., Nichols, D.J., Norris, R.D., Pierazzo, E., Ravizza, G., Rebolledo-Vieyra, M., Reimold, W.U., Robin, E., Salge, T., Speijer, R.P., Sweet, A.R., Urrutia-Fucugauchi, J., Vajda, V., Whalen, M.T., Willumsen, P.S., 2010. The Chicxulub asteroid impact and mass extinction at the Cretaceous-Paleogene boundary. *Science* (80-.). 327, 1214–1218. <https://doi.org/10.1126/science.1177265>
- Simonetti, A., Bell, K., Viladkar, S.G., 1995. Isotopic data from the Amba Dongar Carbonatite Complex, west-central India: Evidence for an enriched mantle source. *Chem. Geol.* 122, 185–198. [https://doi.org/10.1016/0009-2541\(95\)00004-6](https://doi.org/10.1016/0009-2541(95)00004-6)
- Simonov, V.A., Vasil'ev, Y.R., Stupakov, S.I., Kotlyarov, A. V., Karmanov, N.S., 2016. Petrogenesis of dunites of the Guli ultrabasic massif (northern Siberian Platform). *Russ.*

- Geol. Geophys. 57, 1696–1715. <https://doi.org/10.1016/j.rgg.2016.04.009>
- Sobolev, S. V., Sobolev, A. V., Kuzmin, D. V., Krivolutsкая, N.A., Petrunin, A.G., Arndt, N.T., Radko, V.A., Vasiliev, Y.R., 2011. Linking mantle plumes, large igneous provinces and environmental catastrophes. *Nature* 477, 312–316. <https://doi.org/10.1038/nature10385>
- Sprain, C.J., Renne, P.R., Vanderkluysen, L., Pande, K., Self, S., Mittal, T., 2019. The eruptive tempo of Deccan volcanism in relation to the Cretaceous-Paleogene boundary. *Science* (80-). 363, 866–870. <https://doi.org/10.1126/science.aav1446>
- Srivastava, R.K., 1997. Petrology, geochemistry and genesis of rift-related carbonatites of Ambadungar, India. *Mineral. Petrol.* 61, 47–66. <https://doi.org/10.1007/BF01172477>
- Sun, S. -s., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geol. Soc. London, Spec. Publ.* 42, 313–345. <https://doi.org/10.1144/GSL.SP.1989.042.01.19>
- Svensen, H., Planke, S., Polozov, A.G., Schmidbauer, N., Corfu, F., Podladchikov, Y.Y., Jamtveit, B., 2009. Siberian gas venting and the end-Permian environmental crisis. *Earth Planet. Sci. Lett.* 277, 490–500. <https://doi.org/10.1016/j.epsl.2008.11.015>
- Toyoda, K., Horiuchi, H., Tokonami, M., 1994. Dupal anomaly of Brazilian carbonatites: Geochemical correlations with hotspots in the South Atlantic and implications for the mantle source. *Earth Planet. Sci. Lett.* 126, 315–331. [https://doi.org/10.1016/0012-821X\(94\)90115-5](https://doi.org/10.1016/0012-821X(94)90115-5)
- Tucker, J.M., Hauri, E.H., Pietruszka, A.J., Garcia, M.O., Marske, J.P., Trusdell, F.A., 2019. A high carbon content of the Hawaiian mantle from olivine-hosted melt inclusions. *Geochim. Cosmochim. Acta* 254, 156–172. <https://doi.org/10.1016/j.gca.2019.04.001>
- Vasil'Ev, Y.R., Gora, M.P., 2012. The origin of dunites and olivinites in the alkali-ultrabasic intrusive complexes of the Siberian Craton. *Dokl. Earth Sci.* 442, 36–39. <https://doi.org/10.1134/S1028334X12010321>
- Viladkar, S.G., Schidlowski, M., 2000. Carbon and Oxygen Isotope Geochemistry of the Amba Dongar Carbonatite Complex, Gujarat, India. *Gondwana Res.* 3, 415–424. [https://doi.org/10.1016/S1342-937X\(05\)70299-9](https://doi.org/10.1016/S1342-937X(05)70299-9)
- Weidendorfer, D., Schmidt, M.W., Mattsson, H.B., 2017. A common origin of carbonatite magmas. *Geology* 45, 507–510. <https://doi.org/10.1130/G38801.1>
- White, R.S., McKenzie, D., 1995. Mantle plumes and flood basalts. *Journal of Geophysical Research: Solid Earth* 100, 17543–17585. <https://doi.org/10.1029/95jb01585>
- Wilson, G.P., 2014. Mammalian extinction, survival, and recovery dynamics across the Cretaceous-Paleogene boundary in northeastern Montana, USA. *Spec. Pap. Geol. Soc. Am.* 503, 365–392. [https://doi.org/10.1130/2014.2503\(15\)](https://doi.org/10.1130/2014.2503(15))
- Yegorov, L.S., 1989. Form, structure and development of the guli ultramafic-alkalic and carbonatite pluton. *Int. Geol. Rev.* 31, 1226–1239. <https://doi.org/10.1080/00206818909465975>

Tables and Figures

LIP	Carbonatite Province	Age (Ma)	Mean $\delta^{13}\text{C}$	# of samples	References
Deccan	Amba Dongar	[Ar-Ar] 65 ± 0.3	-4.1	13	(Ray and Ramesh, 1999a)
		<i>K-Ar</i>	-4.0	3	(Simonetti et al., 1995)
		<i>K-Ar</i>	-3.8	4	(Srivastava, 1997)
		“currently accepted... late stages of Deccan volcanism”	-2.7	1	(Viladkar and Schidlowski, 2000)
	Mundwara	[Ar-Ar] 68.53 ± 0.22	-5.7	7	(Ray and Ramesh, 1999a)
	Sarnu-Dandali	[Ar-Ar] 68.57 ± 0.08	-5.3	6	(Ray and Ramesh, 1999a)
Paraná-Etendeka	Damara Belt	[Rb-Sr / Ar-Ar] 137-124	-4.3	1	(Le Roex and Lanyon, 1998)
	Araxa	<i>K-Ar</i>	-6.9	1	(Santos and Clayton, 1995)
	Ponta Grossa	[Rb-Sr] 128 ± 19	-6.2	19	(Ruberti et al., 2002)
	Mato Preto	<i>K-Ar</i>	0	1	(Santos and Clayton, 1995)
	Anitápolis	<i>K-Ar</i> (<i>in Spanish</i>)	-7.2	5	(Comin-Chiaramonti et al., 2002)
		<i>K-Ar</i>	-6.7	1	(Toyoda et al., 1994)
	Jacupiranga	<i>K-Ar</i>	-6.1	9	(Morikiyo et al., 1990)
		<i>None given</i>	-6.6	2	(Haynes et al., 2002)
		<i>K-Ar</i>	-6.3	4	(Santos and Clayton, 1995)
		<i>K-Ar</i>	-6.2	2	(Toyoda et al., 1994)
	Catalão	<i>K-Ar</i>	-5.9	1	(Morikiyo et al., 1990)
		<i>K-Ar</i>	-6.5	4	(Santos and Clayton, 1995)
	Sulima-Monte Verde	[Rb-Sr] 130.8 ± 1.4	-5.1	5	(Alberti et al., 1999)
	Bailundo	[Rb-Sr / Ar-Ar] 137-124	-4.9	1	
	Coola		-4.8	1	
	Tchivira-Bonga		-4.2	2	
	Lupongola		-8.1	3	

Table 1. Additional carbonatite isotope data from the Geochemistry of Rocks of the Oceans and Continents (GEOROC) database.

Figure 1A. Map of the Siberian Traps, and the location of the Guli massif (after Malich et al., 1974 and Svensen et al., 2009). **B.** Map of provinces and categories of the Guli Massif of the Maymecha-Kotuy region (after Yegorov, 1989). White dots show where carbonatites were sampled. Red box indicates area represented in Figure 3.

Figure 2. A timeline of the Guli massif emplacement relative to the end-Permian mass extinction.

Figure 3. Representative photos of Guli massif carbonatites that were part of this study. **A.** Carbonatite cores, unlabeled but most likely from the northern carbonatite complex (see Figures 1 & 3; caribou tooth for scale). **B.** Outcrop from the northern carbonatite complex, from locality G08-39 (rock hammer for scale). **C.** Thin section of carbonatite G08-06 from the southern complex.

Figure 4. Spatial distribution of carbonatites sampled from the Guli massif and their corresponding $\delta^{13}\text{C}$ values. Latitude and longitude are given in decimal degrees. Darkest green circles have the lowest $\delta^{13}\text{C}$; yellow circles have the highest.

Figure 5. The $\delta^{13}\text{C}$ of diamonds and large igneous province (LIP) carbonatites, as compared to canonical mantle values. Diamond data after Cartigny et al. (2014). Paraná-Etendeka and Deccan carbonatite data compiled from the GEOROC database. Siberian carbonatite data from this study. Gray shaded region shows the range of mantle $\delta^{13}\text{C}$. Diamond data extends down to -44‰ $\delta^{13}\text{C}$, but the counts are too low to be visible at this scale.

Figure 6. Isotopic ratios of carbon and oxygen in three different large igneous provinces.

Siberian data are from this study (black dots). Deccan and Paraná-Etendeka data (green and orange dots respectively) are compiled from the GEOROC database. Siberian Traps data show 1σ error bars, where they are large enough to be seen, calculated as the standard deviation of the repeat measurements for each sample. Typical mantle values are represented by the orange shaded box. The mean $\delta^{13}\text{C}$ values for each LIP are shown at the top of the graph, with bars showing one standard error.

Figure 7. A. Rare Earth Element (REE) profiles of Guli carbonatites, normalized to chondrite values (McDonough and Sun, 1995). Shades of the lines represent relative $\delta^{18}\text{O}$, with darker lines representing higher values. Mid-ocean ridge basalt and ocean island basalt (MORB and OIB; Sun and McDonough, 1989) profiles included for comparison. Beneath are subsets showing different characteristics: **B.** Steep, near-linear enrichment patterns, belonging to the southern carbonatite complex of the study area; **C.** Patterns with steep initial declines followed by a plateau, belonging to the northern complex (see Figure 4).

Figure 8. Carbon isotope evolution of dissolved and exsolved carbon in a recharging, crystallizing, and erupting magma reservoir. **A.** For recharging magma containing 2000 ppm CO_2 , assuming a carbon solubility of 500 ppm CO_2 (thin lines) or 2000 ppm CO_2 (thick lines). We assume a fluid-melt carbon isotope fractionation factor of +4.25‰ (Gerlach and Taylor, 1990; Javoy et al., 1978) **B.** For comparison, the overall distribution of $\delta^{13}\text{C}$ in carbonatites from the Siberian Traps, Deccan Traps, and Paraná-Etendeka Traps. **C.** An eruption is assumed to take place when the chamber mass increases by 10%. During each eruption we assume that all exsolved CO_2 is released.