



Carbonatites and Global Tectonics

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Carbonatites have formed for at least the past three billion years. But over the past 700 My the incidence of carbonatites have significantly increased. We compile an updated list of 609 carbonatite occurrences and plot 387 of known age on plate tectonic reconstructions. Plate reconstructions from Devonian to present show that 75% of carbonatites are emplaced within 600 km of craton edges. Carbonatites are also associated with large igneous provinces, orogenies, and rift zones, suggesting that carbonatite magmatism is restricted to discrete geotectonic environments that can overlap in space and time. Temporal constraints indicate carbonatites and related magmas may form an ephemeral but significant flux of carbon between the mantle and atmosphere.

KEYWORDS: carbonatites; global tectonics; mantle carbon; cratons; LIPs; orogenic magmatism

INTRODUCTION

Magmas parental to carbonatites have been generated for at least two-thirds of Earth's history: the oldest known carbonatite is the Mesoarchean 3.01 Ga carbonatite Tupertalik in Greenland (Bizzarro et al. 2002). The only currently active carbonatite volcano is Oldoinyo Lengai (Tanzania), which erupts alkali-rich carbonatite and is unique within the rock record (excluding compositionally similar minerals and melt inclusions). Carbonatites are largely confined to the continental lithosphere (FIG. 1) with a few examples occurring on older, thicker, oceanic lithosphere, associated with ocean island basalt (OIB) volcanism. Carbonatites occur in a variety of tectonic settings, including stable intraplate areas and in association with rifts, lithospheric highs, and orogenies (Woolley 1989; Simandl and Paradis 2018). The emplacement of carbonatites is largely continuous throughout Earth's history from 3 Ga, but exhibits a significant increase in the number of occurrences with time (FIG. 2) (Woolley 1989; Woolley and Kjarsgaard 2008; Kogarko and Veselovskiy 2019).

Carbonatites are the products of low-degree partial melting of an enriched (relative to ambient upper mantle) or metasomatised mantle. Mantle metasomatism is the sub-solidus chemical change of a rock and is observed in much of the continental lithospheric mantle. Carbonatites may be directly erupted from their mantle source or, more frequently, emplaced after protracted modification within the lithosphere (Woolley and Kjarsgaard 2008). Carbonatites are diverse rocks formed through eruption,

intrusion, or carbohydrothermal fluid activity (Mitchell 2005; Woolley and Kjarsgaard 2008). Isotopic studies of selected carbonatites may indicate a temporally isolated mantle source for the magmas (Nelson et al. 1988; Bell and Simonetti 2010), and their association with large igneous provinces (LIPs) has been used to suggest an association with deep mantle phenomena (Ernst and Bell 2010).

The number of carbonatites through time is an expression of how their mantle source conditions have changed, combined with the effects of selective preservation in the geological record. Carbonatites require specific physico-chemical conditions within the asthenospheric and/or lithospheric mantle source to generate their parental low-degree melts, but they also require favourable tectonic regimes to promote transport of such low-volume melts through the lithosphere.

The contribution of carbonatites as a flux of carbon between the mantle and the atmosphere has historically been regarded as insignificant due to the rarity of carbonatites (e.g., Woolley 1989) and the low volume of carbonatite magmatism at any one occurrence. However, recent work suggests carbonate-rich magmas may be important in transporting carbon from the mantle to the atmosphere (Foley and Fischer 2017; Paulsen et al. 2017; Yaxley et al. 2019). The recognition of their association with other CO₂-rich magmas suggests that the overall flux of CO₂ may be significant, at least on geologically short timescales.

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We collate an up-to-date list of 609 carbonatites and present a model detailing the distribution of 387 of known age (FIG. 1), which takes into consideration plate-tectonic reconstruction models for the last 410 My. We focus on understanding the relationship between the spatial and temporal occurrences of carbonatites and relevant geotectonic features through time (FIG. 3, the example at 130 Ma). Specifically, we place the history of carbonatite magmatism within the context of the Young et al. (2018) model for tectonic history ~410–250 Ma, which we modified along western North America to improve the kinematic evolution of terrane accretions, linked to data in Müller et al. (2019) for the period 250–0 Ma, and to a newly derived, optimised, mantle reference frame using the open-source GPlates platform (www.gplates.org).

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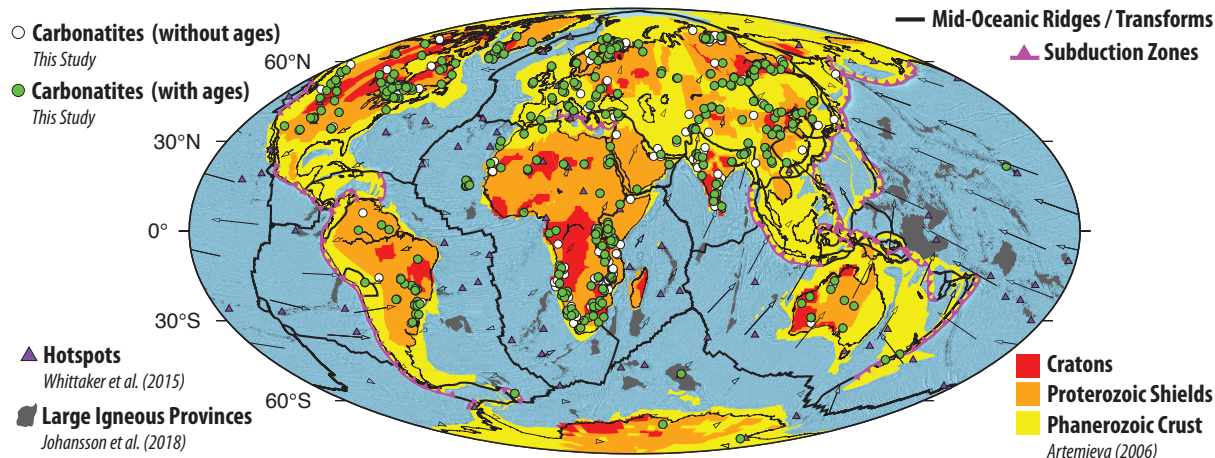


FIGURE 1 The global distribution of carbonatites. For further details and references see supplement.

CARBONATITES AND THE LITHOSPHERE

The close spatial and temporal association of carbonatites with alkaline rocks, along with mineralogical affinities and incompatible element (including light rare earth element) enrichment, suggests a close petrogenetic relationship between the rock types: 76% of known occurrences of carbonatites are associated with some form of alkaline rock (Woolley and Kjarsgaard 2008). Although generally confined to continental areas, some carbonatites occur in oceanic settings (FIG. 1) (Schmidt and Weidendorfer 2018), whereas alkaline rocks are abundant on the continental and the oceanic lithosphere. It is, therefore, possible to generate alkaline magmas from below the sub-oceanic lithosphere, but much rarer to generate carbonatite-forming magmas in oceanic settings.

The association of carbonatites with cratonic lithosphere was recognised from early studies in Africa, but compilations of global datasets showed the association is consistent across all continents (Woolley 1989; Woolley and Kjarsgaard 2008; Simandl and Paradis 2018). Our analysis shows the closest spatial association is between carbonatites and the edges of cratons (FIG. 4). This association may partly reflect the proportion of the continental crust occupied by cratons and their dimensions, but also suggests that the optimal extraction conditions for carbonatites occur along the significant boundaries that exist within the lithosphere between the cratonic and non-cratonic lithosphere.

Carbonatites are often associated with rifts (e.g., Foley and Fischer 2017); however, our data show that only ~25% of carbonatites are found within ~1,000 km of major modern or palaeo-rifts (FIG. 4). Rifting (or extensional tectonic regimes) can be associated with major plate reconfiguration, large igneous province eruption, or may result from more local-scale changes in the stress regime over a plate. Therefore, the factors controlling rifting likely influence the local mantle conditions (e.g., temperature, composition, and depth of the lithosphere–asthenosphere boundary), and, thus, the propensity to generate carbonatite-forming melts.

Continental lithospheric control on carbonatite spatial distribution is demonstrated when examining the repetition of carbonatite occurrences through time. In several regions around the world—including Eastern Africa, Greenland, and Southern Africa—carbonatites are repeatedly emplaced through time (Woolley and Bailey 2012). Foley and Fischer (2017) present modelling of the deep

lithospheric budget of carbon and suggest that the lithosphere acts as a vast store for carbon at depth, both from incipient melts generated from the asthenospheric mantle, which accumulate through time, but also from plume-derived material. Carbon stored at the base of the lithosphere can be remobilised through redox reactions and decompression melting, concentrated in regions dictated by the architecture of the lithosphere–asthenosphere boundary (Foley and Fischer 2017) and the presence, or reactivation, of faults and lineaments in the lithosphere. Carbon-rich regions may then be reactivated repeatedly through time to generate carbonatites, carbon-rich magmatism, and associated degassing.

MANTLE CONDITIONS FOR GENERATING CARBONATITIC MELTS

The mantle conditions required to generate carbonatitic melts are strict. Low-degree melting (<1%) is crucial to matching major and trace element compositions of carbonatites, implying that the mantle temperatures in carbonatite-melt source regions are at, or close to, the CO₂-bearing peridotite (or eclogite) solidus. Carbonatites are not known from the geological record before 3.01 Ga; alkaline rocks appear in the geological record at 2.79 Ga, and kimberlites at ~2.85 Ga (Tappe et al. 2018). This implies either that the physico-chemical conditions required for generating melts parental to carbonatite were not established prior to this time (Woolley 1989; Tappe et al. 2018) or that previously formed rocks have been lost from the geologic record.

Magma volumes, coupled with incompatible element enrichment and metasomatised mantle xenoliths entrained in carbonatitic volcanism, and carbon-rich alkaline volcanic provinces both indicate a metasomatised mantle source region for carbonatitic magmatism (Woolley and Kjarsgaard 2008; Hutchison et al. 2019). Metasomatism of the lithospheric mantle results from the fluxing of low-degree, ephemeral melts that have been derived from the melting of ambient upwelling asthenospheric mantle, from above subducting oceanic lithosphere, and from the peripheries of upwelling thermal anomalies in the mantle. Dating of metasomatic minerals (e.g., amphibole, phlogopite, apatite, sulfides) in mantle xenoliths entrained in carbon-rich magmatism shows the process is dynamic and cumulative over geological time and can both be concurrent with and predate magmatism by many hundreds of millions of years.

Radiogenic isotopic studies (using Sr, Nd, and Pb) of carbonatites have helped to establish that carbonatites are mantle-derived melts (Nelson et al. 1988; Bell and Blenkinsop 1989). The isotopic ratios of carbonatites are distinct from mid-ocean-ridge basalt (MORB, which is assumed to reflect

the isotopic composition of the depleted upper mantle); carbonatites that are younger than 200 Ma are similar to ocean island basalt (OIB) compositions.

Stable isotope studies of carbonatites and alkaline rocks indicate that the mantle source is metasomatised lithosphere or recycled material in mantle plumes (e.g., Hutchison et al. 2019; Amsellem et al. 2020). Hutchison et al. (2019) demonstrate that there is a temporal change in the sulfur isotope composition of sources of alkaline rocks and carbonatites, and this could reflect changes in the composition of the lithospheric mantle and/or billion-year timescales of deep crustal recycling. Amsellem et al. (2020) used Ca isotopes to show that carbonatites have isotopically lighter Ca than basalts and suggest that this is evidence for the recycling of isotopically light sediments into the mantle, creating hybrid carbonatite sources rich in a component of recycled sediment. Carbon isotopes in many carbonatites overlap with the average value of the asthenospheric upper mantle: $\delta^{13}\text{C} \approx -5\text{‰}$ (Deines 2002). Deviations in individual carbonatites are ascribed to either variations in the carbon isotope content of the mantle source of the magmas (e.g., a recycled source component), assimilation of host rocks, post-magmatic hydrothermal fluid flow, or magmatic degassing.

CHANGES IN MANTLE CONDITIONS AND THE GENERATION OF CARBONATITES

Several studies using increasing numbers of carbonatite occurrences of known age (Woolley 1989 [n = 148]; Woolley and Kjarsgaard 2008 [n = 155]; Kogarko and Veselovskiy 2019 [n = 180]; Woolley and Bailey 2012 [n = 274]; this study [n = 387]) have shown an increase in carbonatite abundance through time. This has also been demonstrated for alkaline igneous rocks (Kogarko 1996) and kimberlites (Tappe et al. 2018). The change in abundance of carbonatites with time was initially argued by Woolley (1989) as evidence for a change in the physical conditions of melt-forming regions. The change may also reflect the preservation biases of the geological record. Destruction of the lithosphere (e.g., burial, erosion, and metamorphism) is expected to have some effect on the carbonatite record. However, there is strong evidence to suggest that physical conditions within the lithosphere and asthenosphere have changed with time to promote the generation of small-fraction partial melts, parental to carbonatites. FIGURE 2 details carbonatite occurrences from the Mesoarchean to the present day, including a comparison with an estimate of the proportion of continental crust of Precambrian age, including exposed Precambrian (dark grey) and exposed-plus-buried (light grey) (Goodwin 1996). The estimates of the age of the exposed present-day crust can be taken as a proxy for the preservation record, i.e., the oldest rocks (>650 Ma) form <15% of the total exposed continental crust and, thus, carbonatites older than 650 Ma are equally unlikely to be preserved in the rock record. However, the distribution of carbonatites exhibits greater variability than the current surface area age distribution: for example, the period of 150–500 Ma has less carbonatites, and there are significant “pulses” of carbonatite activity from the Neoproterozoic to present that would not be predicted by surface age distribution alone. Tappe et al. (2018) observe a general increase in the abundance of kimberlites since ~2 Ga (similar to the overall increase in the frequency of carbonatites since 3 Ga) and conclude that the abundance reflects changes in the mantle temperature and oxidation state with time. Thus, preservation is not the sole factor influencing the distribution of carbonatites through time. Other variables must be considered to explain the temporal variation of carbonatites.

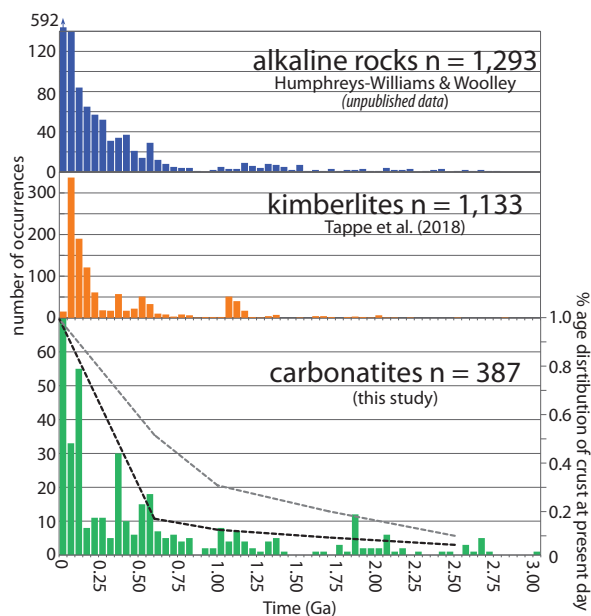


FIGURE 2 Histogram of carbonatites of known age ($n = 387$). Kimberlites and alkaline rock ages shown for comparison; note varying y-axis scales. Dashed lines show percentage age distribution at the present day (dark = exposed; light = exposed plus buried). FROM GOODWIN (1996).

The origin and abundance of carbon within the early Earth was affected by processes, including planetesimal accretion, core formation, giant impacts, the moon-forming impact, and the late veneer of meteoritic material (Dasgupta 2013). The initial concentration of carbon in the Earth’s mantle is affected by volatile loss during planetary accretion and differentiation into the core. Subsequently, due to high temperatures in the early Earth (if the mantle was oxidising enough), much of the mantle would be at or above the carbonated peridotite solidus and, therefore, carbon would be rapidly extracted and lost to the atmosphere and/or space. The late veneer of meteorites likely increased the concentration of carbon in the mantle. Continued modification of the carbon concentration of the mantle results from the balance of carbon subducted into the deep mantle and carbon degassed from volcanism. The effectiveness of both the incorporation of carbon and how quickly it is outgassed from the mantle is dependent on mantle temperature and availability of oxygen (due to its effect on the speciation of carbon). Dasgupta (2013) suggests that in the hotter, early (Hadean) Earth, subduction would have been an ineffective way of transporting carbon into the deep mantle, and most carbonate would have been driven from the subducting slab through the volcanic arc. At the same time, a high potential temperature of the mantle (T_p – the temperature the mantle would have at Earth’s surface if ascending without transferring heat or mass) would have also promoted carbonate-assisted peridotite melting such that carbon would be more effectively degassed from the mantle. It is, therefore, only with secular mantle cooling that subduction zones could become more effective transporters of carbon to the deep mantle, and the mantle potential temperature would drop below the carbonated peridotite solidus.

The ability of the mantle to retain carbon is also bound to the oxidation state of the mantle, where reduced carbon phases (such as graphite, diamond, and methane) act as long-term repositories for carbon. Prior to 3 Ga, it is unclear what the oxidation state of the Earth’s mantle was: some evidence suggests more reducing than present, other evidence suggests a stable mantle oxidation state since the

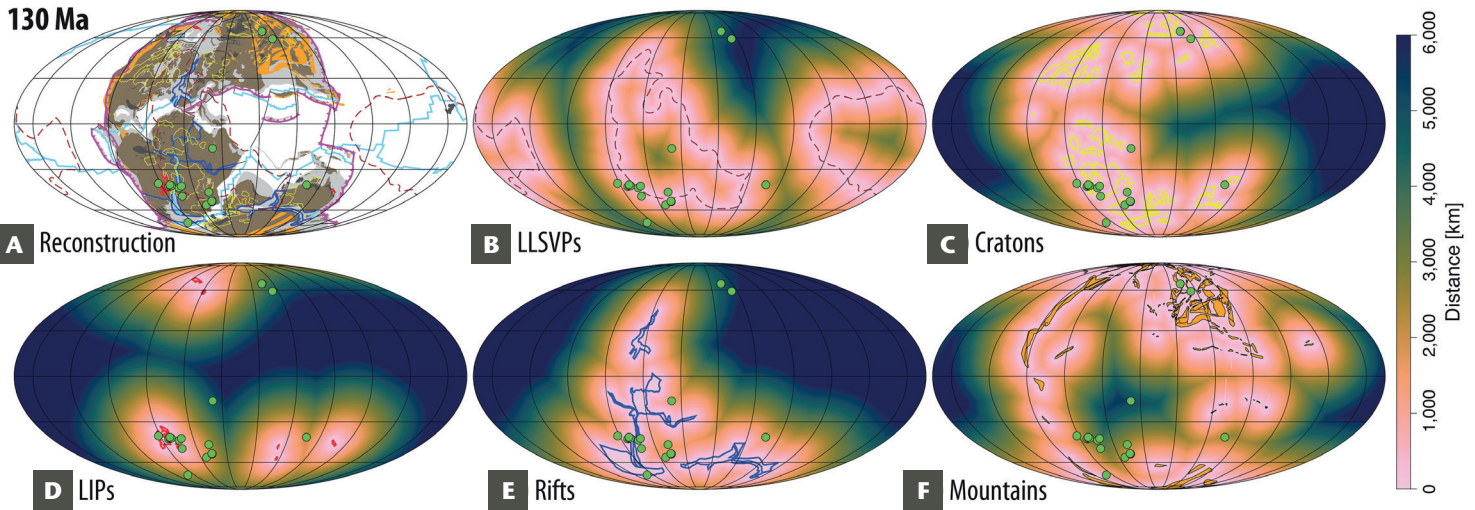


FIGURE 3 (A) Global plate tectonic reconstruction for 130 Ma with carbonatite-forming events as green circles (and note green circle distributions on the following diagrams). MODIFIED AND MERGED MODELS OF YOUNG ET AL. (2018) AND MÜLLER ET AL. (2019). (B) Present-day large low shear-wave velocity province (LLSVP) outlines; note -0.7% S-wave velocity anomaly contour. FROM DAVIES ET AL. (2015). (C) Present-day craton distribu-

tion. (D) Present-day mantle-plume volcanic products from large igneous provinces (LIPs). AFTER JOHANSSON ET AL. (2018). (E) Present-day active major rifts at a given time interval. (F) Present-day orogenies (mountain building). AFTER CAO ET AL. (2017). Spherical distance grids generated using Generic Mapping Tools and intersected with carbonatite occurrences. FOR FURTHER DETAILS AND REFERENCES SEE SUPPLEMENT.

Eoarchean and further evidence suggests that the Archean mantle oxidation state may have been highly heterogeneous. The input of carbon into the mantle through subduction zones is also likely to have varied significantly due to the episodic nature of hot, early subduction and the variability of carbon-rich sediments on the Earth's surface.

A range of geological indicators can be used to predict when and where in the early Earth melts parental to carbonatites could have formed. The Earth's mantle has experienced secular cooling since the Archean (Dasgupta 2013 and references therein). Because carbonatites are largely confined to the continental lithosphere, the formation and stabilisation of the continental lithosphere can also be used to constrain the initiation of carbonatitic magmatism. The potential for subduction of increasing volumes of carbon into the deep mantle, and continued cumulative metasomatism of the lithospheric mantle, coupled with a potential change in mantle oxygen fugacity, suggests that the physico-chemical parameters required for the generation of carbonatitic melts have become more prevalent with time.

CARBONATITES AND THE (DEEP) MANTLE

Large igneous provinces (LIPs) are often attributed to mantle plumes with a deep mantle origin, based on evidence from primordial isotopic ratios (e.g., $^3\text{He}/^4\text{He}$). The impact of a plume on the lithosphere generates a large volume ($>10^6$ – 10^5 km³) of magma, typically forming flood basalts and some minor felsic magmatism, within geologically short timescales (0.1–1 My). There are temporal and spatial correlations between LIPs and carbonatites, which date back as far as 2.06 Ga (Bushveld Igneous Complex, South Africa) (Ernst and Bell 2010). Depending on the LIP thermal regime, carbonatites have been documented to occur prior to, during, or after LIP magmatism. Our data show a weak temporal and spatial correlation between carbonatites and LIPs (FIG. 4) which may be explained by the relatively short duration of the active LIP magmatism in our models versus the much longer heating of the lithosphere that enables the generation of carbonatitic melts pre- and post-LIP magmatism.

Kogarko and Veselovskiy (2019) modelled the emplacement of 155 carbonatites on plate reconstructions to show the spatial association between selected carbonatites and a large low shear-wave velocity province (LLSVP) at the core–mantle boundary. The reconstructions show that 66% of the carbonatites studied can be linked to one LLSVP largely beneath Africa; however, the other significant LLSVP (which currently resides under the Pacific Ocean) was not linked to any carbonatites, and the remaining 34% were not associated with either LLSVP. Our data show that there is a spatial relationship between present-day LLSVP outlines and carbonatites (FIG. 4), but it is not as strong as other geotectonic settings studied (e.g., cratons and orogens). Our approach also assumes fixed and unchanging LLSVPs through time, which is likely an oversimplification. The LLSVPs have been linked to plumes, and the association with carbonatites may be valid where they can be linked to both an LLSVP and LIP magmatism.

Kimberlites are arguably related to carbonatites (particularly the rapidly erupted, diatremic carbonatites) in that both are formed from low-degree melts of metasomatised mantle. Kimberlites are largely confined to the cratons, and some have entrained diamonds containing high-pressure mineral inclusions that indicate an origin from deep

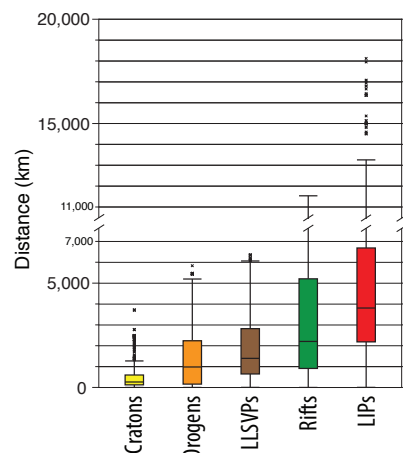


FIGURE 4 Box-and-whisker plots of the pooled distances from carbonatite occurrences to each tectonic setting over the model timeframe of 410 Ma to 0 Ma. Note that 75% of all carbonatites erupt within ~ 600 km of craton edges, within $\sim 2,200$ km of orogenies, within $\sim 2,800$ km of large low shear-wave velocity province (LLSVP) edges, within $\sim 5,200$ km of active rifts, and within $\sim 6,700$ km of erupting plume products (large igneous provinces, LIPs). FOR FURTHER DETAILS AND REFERENCES SEE SUPPLEMENT.

within the mantle. However, Tappe et al. (2020) studied the tungsten isotope composition of a variety of kimberlites across Africa, which have been linked to plumes and the LLSVP, finding that kimberlites across Africa do not carry a primitive or LLSVP signature: instead, they have tungsten isotopic compositions that are indistinguishable from modern ambient mantle (i.e., a depleted MORB source).

Melts parental to carbonatites can be generated in the sub-lithospheric mantle (see Timmerman et al. 2021 this issue; Yaxley et al. 2021 this issue and references therein). These asthenosphere-derived melts (FIG. 5) are likely to be the source for both the metasomatism of the lower lithospheric mantle and a potential heat source for melting metasomatised lithosphere, or the parental melts to carbonatite magmas themselves. However, the extent to which most carbonatitic melts have interacted with the lithosphere on ascent means that tracing this original source is extremely challenging.

THE ROLE OF CARBONATITES IN THE GLOBAL CARBON CYCLE

Carbonatites have historically been considered unusual, rare rocks that are confined to stable intraplate areas. However, we know them to occur across a range of lithosphere types and to be associated with CO₂-rich alkaline magmas and mantle source regions. There are at least 609 carbonatites and, when considered with carbon-rich alkaline rocks (n = 2,586) (Humphreys-Williams and Woolley, unpublished data) and kimberlites (n = ~5,652) (Tappe et al. 2018), there are around 8,847 occurrences of CO₂-rich magmatic rocks. This is a conservative estimate because collations often contain complexes or volcanic fields as one entry and the geological record is incomplete; thus, a complete count of such CO₂-rich igneous rocks would underestimate their production over Earth history. The CO₂-rich magmatism (although volumetrically small in many cases) is associated with significant degassing of mantle-derived CO₂ both pre- and post-volcanism. Carbonatites and related rocks also contribute to the flux of carbon from the mantle to the lithosphere through magmas that intrude the lithosphere but that fail to erupt. As proposed by Sleep (2009), kimberlite melts which fail to reach the Earth's surface have been frozen in the deep lithosphere, so forming a significant CO₂ reservoir. It is entirely plausible that a whole spectrum of CO₂-rich small-fraction partial melts (alkaline, carbonatitic, kimberlitic) may be trapped in the lithosphere and that carbonate-rich metasomatism may be near-ubiquitous in the deep lithospheric mantle.

Due to degassing, igneous rocks do not retain a reliable record of the CO₂ budget of the primitive magmas from which they were derived, and carbonatites are no exception. Despite carbonate minerals being stable and crystallising a proportion of the magmatic CO₂, much more is expected to be lost either through magmatic degassing, fenite-forming processes, and/or decarbonation reactions. Paulsen et al. (2017) provide evidence for the impact of CO₂ derived from carbonatitic and alkaline magmatism and demonstrate that there is a temporal correlation between a proposed mantle cooling event prior to the Ediacaran and a subsequent spike in carbonatitic and alkaline magmatism (as determined through detrital zircon chemistry), which then led to an increase in volcanic CO₂ and so promoted global warming. Degassing of CO₂ from active rift environments associated with carbonatites is higher than previously thought (Foley and Fischer 2017). Other regions, such as small monogenetic volcanic fields containing carbonatites and other carbon-rich alkaline basaltic magmas, may also have a significant role in the carbon flux from the mantle to the crust and atmosphere. Carbon-rich alkali basaltic magmas typically erupt as volumetrically small products (maars or cinder cones) but are associated with passive degassing of mantle-derived CO₂ for millions of years past the cessation of volcanism. This volcanism typically entrains xenoliths of highly metasomatised mantle, suggesting parts of the non-cratonic lithosphere (away from major rifts) contain significant stores of CO₂, which is released when lithospheric stress regimes permit. The impact of CO₂ degassing at such volcanic fields has not been considered in long-term estimates of carbon degassing from the mantle due to poor constraints on the flux of CO₂ from these fields and due to the relatively recent acknowledgement of carbonatitic volcanism in these provinces. Critically, it may be possible that the impact of carbon-rich magmatism on the atmospheric concentrations of CO₂ may be enhanced when the relevant geotectonic environments (FIG. 5) happen simultaneously, optimising the flux of CO₂ from the mantle to the atmosphere.

SUMMARY

Carbonatites are derived from low-degree partial melting of an enriched or metasomatised mantle source and are either directly erupted or experience varying degrees of magmatic modification or low-temperature alteration after emplacement or eruption. The increase in carbonatites, alkaline rocks, and kimberlites with time is likely a result of mantle cooling over Earth's history, the formation and stabilisation of the lithosphere, compositional change of the mantle due to subduction, and the cumulative effect

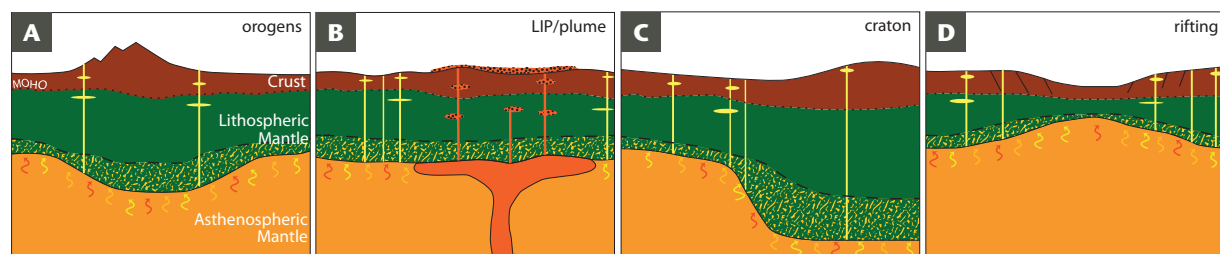


FIGURE 5 Schematic of the most common geotectonic settings of carbonatite magmatism. Note that no temporal relationship between the geotectonic event and the formation of carbonatite magmatism is given, i.e., carbonatite magmatism may happen at any time during the event or may be restricted to discrete periods. Textured area within lithospheric mantle represents regions where cumulative metasomatism at the base of the lithosphere may occur. Wiggly arrows denote asthenosphere-derived, carbon-rich metasomatic melts of varying chemical composition, which may be parental to carbonatitic magmatism, may induce melting, or metasomatise the lithosphere. Vertical lines detail the path of carbonate-rich melts; those with spots are large igneous province (LIP) basalts and related rocks.

(A) Carbonatite magmatism in orogens: where lithospheric stress regime is favourable, carbonatites may be erupted or emplaced. (B) Carbonatites associated with LIP and mantle plumes: carbonatites are typically generated on the periphery of the flood basalts and/or temporally early or late. (C) Carbonatite emplacement in cratons: carbonatites are strongly associated with the edges of cratons where the lithospheric features make it easier for the traversing melts and where volatiles may be concentrated due to the LAB (lithosphere–asthenosphere boundary) topography. (D) Carbonatites erupting around the margin of rifted settings where mantle melting conditions are suitable, i.e., incompatible elements are enriched and melting can occur at low melt fractions.

of metasomatism of the lithospheric mantle through time. Our spatio-temporal analysis suggests a strong association between craton edges and carbonatite occurrences (FIG. 4). This may suggest that most continental regions where carbonatites form have some Archean cratonic component, but carbonatites are also an outcome of the conditions necessary for deep lithospheric carbon storage and mobilisation into carbonatite-forming melts. Many carbonatites throughout Africa and South America can be spatially linked to an LLSVP, but there are no known carbonatites above the Pacific LLSVP, suggesting that the nature of the lithosphere (i.e., continental vs. oceanic), and not the deep mantle, is critical in carbonatite genesis.

Three optimal conditions for the generation of carbonatite-forming magmas can be outlined as follows: 1) near-solidus mantle temperatures and a C-rich metasomatised mantle source; 2) extended periods of time to accumulate carbon within the lithosphere; 3) geotectonic event(s) forming appropriate lithospheric stress regimes to mobilise C-rich regions or allow the ascent of C-rich melts.

The impact of carbonatitic (and associated alkaline) magmatism on the global carbon cycle is beginning to be recognised, but passive degassing around intraplate volcanic fields requires further attention. New methods for monitoring carbonatite and alkaline rock distribution through time (such as detrital zircon studies), and further constraints on the volumes of carbon emitted by carbonatites, alkaline rocks, and associated degassing,

potentially over geologically short time periods, will help to illustrate the importance of carbonatites for the transport and storage of carbon between the mantle and the atmosphere and their influence on the global carbon cycle over geological time.

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REFERENCES

- Amsellem E and 6 coauthors (2020) Calcium isotopic evidence for the mantle sources of carbonatites. *Science Advances* 6: eaba326, doi: 10.1126/sciadv.aba3269
- Bell K, Simonetti A (2010) Source of parental melts to carbonatites—critical isotopic constraints. *Mineralogy and Petrology* 98: 77–89, doi: 10.1007/s00710-009-0059-0
- Bizzarro M, Simonetti A, Stevenson RK, David J (2002) Hf isotope evidence for a hidden mantle reservoir. *Geology* 30: 771–774 doi: 10.1130/0091-7613(2002)030<0771:HIEFA H>2.0.CO;2
- Cao W and 5 coauthors (2017) Improving global paleogeography since the late Paleozoic using paleobiology. *Biogeosciences* 14: 5425–5439, doi: 10.5194/bg-14-5425-2017
- Dasgupta R (2013) Ingassing, storage, and outgassing of terrestrial carbon through geologic time. *Reviews in Mineralogy and Geochemistry* 75:183–229, doi: 10.2138/rmg.2013.75.7
- Davies DR, Goes S, Sambridge M (2015) On the relationship between volcanic hotspot locations, the reconstructed eruption sites of large igneous provinces and deep mantle seismic structure. *Earth and Planetary Science Letters* 411: 121–130, doi: 10.1016/j.epsl.2014.11.052
- Deines P (2002) The carbon isotope geochemistry of mantle xenoliths. *Earth-Science Reviews* 58: 247–278, doi: 10.1016/S0012-8252(02)00064-8
- Ernst RE, Bell K (2010) Large igneous provinces (LIPs) and carbonatites. *Mineralogy and Petrology* 98: 55–76; doi: 10.1007/s00710-009-0074-1
- Foley SF, Fischer TP (2017) An essential role for continental rifts and lithosphere in the deep carbon cycle. *Nature Geoscience* 10: 897–902, doi: 10.1038/s41561-017-0002-7
- Goodwin AM (1996) *Principles of Precambrian Geology*. Academic Press, San Diego, 327 pp, doi: 10.1016/B978-0-12-289770-2.X5000-6
- Hutchison W and 9 coauthors (2019) Sulphur isotopes of alkaline magmas unlock long-term records of crustal recycling on Earth. *Nature Communications* 10: 4208, doi: 10.1038/s41467-019-12218-1
- Johansson L, Zahirovic S, Müller RD (2018) The interplay between the eruption and weathering of large igneous provinces and the deep-time carbon cycle. *Geophysical Research Letters* 45: 5380–5389, doi: 10.1029/2017GL076691
- Kogarko LN (1996) Alkaline magmatism and enriched mantle reservoirs: mechanisms, time, and depth of formation. *Geochemistry International* 44: 3–10, doi: 10.1134/S0016702906010022
- Kogarko LN, Veselovskiy RV (2019) Geodynamic origin of carbonatites from the absolute palaeotectonic reconstructions. *Journal of Geodynamics* 125: 13–21, doi: 10.1016/j.jog.2019.01.017
- Mitchell RH (2005) Carbonatites and carbonatites and carbonatites. *Canadian Mineralogist* 43: 2049–2068, doi: 10.2113/gscanmin.43.6.2049
- Müller RD and 13 coauthors (2019) A global plate model including lithospheric deformation along major rifts and orogens since the Triassic. *Tectonics* 38: 1884–1907, doi: 10.1029/2018TC005462
- Nelson DR, Chivas AR, Chappell BW, McCulloch MT (1988) Geochemical and isotopic systematics in carbonatites and implications for the evolution of ocean-island sources. *Geochimica et Cosmochimica Acta* 52: 1–17, doi: 10.1016/0016-7037(88)90051-8
- Paulsen T, Deering C, Sliwinski J, Bachmann O, Guillong M (2017) Evidence for a spike in mantle carbon outgassing during the Ediacaran period. *Nature Geoscience* 10: 930–934, doi: 10.1038/s41561-017-0011-6
- Schmidt MW, Weidendorfer D (2018) Carbonatites in oceanic hotspots. *Geology* 46: 435–438, doi: 10.1130/G39621.1
- Simandl GJ, Paradis S (2018) Carbonatites: related ore deposits, resources, footprint, and exploration methods. *Applied Earth Science* 127: 123–152, doi: 10.1080/25726838.2018.1516935
- Sleep NH (2009) Stagnant lid convection and carbonate metasomatism of the deep continental lithosphere. *Geochemistry, Geophysics, Geosystems* 10: Q11010, doi: 10.1029/2009GC002702
- Tappe S, Budde G, Stracke A, Wilson A, Kleine T (2020) The tungsten-182 record of kimberlites above the African superplume: exploring links to the core-mantle boundary. *Earth and Planetary Science Letters* 547: 116473, doi: 10.1016/j.epsl.2020.116473
- Tappe S, Smart K, Torsvik T, Massuyeau M, de Wit M (2018) Geodynamics of kimberlites on a cooling Earth: clues to plate tectonic evolution and deep volatile cycles. *Earth and Planetary Science Letters* 484: 1–14, doi: 10.1016/j.epsl.2017.12.013
- Timmerman S, Spivak A, Jones A (2021) Carbonatitic melts and their role in diamond formation in the deep Earth. *Elements* 17: 321–326
- Woolley AR (1989) The spatial and temporal distribution of carbonatites. In: Bell K (ed) *Carbonatites: Genesis and Evolution*. Unwin Hyman Ltd, London, pp 15–37
- Woolley AR, Bailey DK (2012) The crucial role of lithospheric structure in the generation and release of carbonatites: geological evidence. *Mineralogical Magazine* 76: 259–270, doi: 10.1180/minmag.2012.076.2.02
- Woolley AR, Kjarsgaard BA (2008) Paragenetic types of carbonatite as indicated by the diversity and relative abundances of associated silicate rocks: evidence from a global database. *Canadian Mineralogist* 46: 741–752 doi: 10.3749/canmin.46.4.741
- Yaxley G and 6 coauthors (2019) CO₂-rich melts in the Earth. In: Orcutt BN, Daniel I, Dasgupta R (eds) *Deep Carbon Past to Present*. Cambridge University Press, Cambridge, pp 129–162, doi: 10.1017/9781108677950
- Yaxley G, Kjarsgaard BA, Jaques AL (2021) Upper mantle to crustal evolution of carbonatite magmas. *Elements* 17: 315–320
- Young A and 6 coauthors (2018) Global kinematics of tectonic plates and subduction zones since the late Paleozoic Era. *Geoscience Frontiers* 10: 989–1013, doi: 10.1016/j.gsf.2018.05.011 ■