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Carbonatites: Classification, Sources, Evolution, and Emplacement

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carbonatite, silicate-carbonate liquid immiscibility, fenitization, antiskarns, rare earth elements, recycled crust, Oldoinyo Lengai

Abstract

Carbonatites are igneous rocks formed in the crust by fractional crystallization of carbonate-rich parental melts that are mostly mantle derived. They dominantly consist of carbonate minerals such as calcite, dolomite, and ankerite, as well as minor phosphates, oxides, and silicates. They are emplaced in continental intraplate settings such as cratonic interiors and margins, as well as rift zones, and rarely on oceanic islands. Carbonatites are cumulate rocks, which are formed by physical separation and accumulation of crystals that crystallize from a melt, and their parental melts form by either (*a*) direct partial melting of carbonate-bearing, metasomatized, lithospheric mantle producing alkali-bearing calcic dolomitic melts or (*b*) silicate-carbonate liquid immiscibility following fractional crystallization of carbonate-bearing, silica-undersaturated magmas such as nephelinites, melilitites, or lamprophyres. Their emplacement into the crust is usually accompanied by fenitization, alkali metasomatism of wallrock caused by fluids expelled from the crystallizing carbonatite.

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Carbonatites are major hosts of deposits of the rare earth elements and niobium, and the vast majority of the global production of these commodities is from carbonatites.

- Carbonatites are igneous rocks formed from carbonate-rich magmas, which ultimately formed in Earth's upper mantle.
- Carbonatites are associated with economic deposits of metals such as the rare earth elements and niobium, which are essential in high-tech applications.
- There are more than 600 carbonatites in the geological record but only one currently active carbonatite volcano, Oldoinyo Lengai in Tanzania.

Rare earth elements (REE): yttrium and the 14 naturally occurring lanthanides from La to Lu; scandium is not considered a REE

Carbonatite system: all igneous and metasomatic rocks, melts, and fluids and their mutual interaction processes and products at any particular carbonatite occurrence

Ankerite: in the carbonatite literature, an informal term for any dolomite with substantial Fe contents, including compositions with $Mg\# > 0.5$ [$Mg\# = Mg/(Mg + Fe)$]

Natrocarnatite: an evolved carbonatite melt or rock comprising dominantly alkali carbonates (nyerereite and gregoryite) with halogen enrichment

1. INTRODUCTION

Carbonatites are perplexing igneous rocks, consisting mostly of carbonate minerals, that have been emplaced into Earth's crust or erupted onto its surface in a variety of tectonic settings since the Archean (Humphreys-Williams & Zahirovic 2021). There is a long history of academic and economic interest in carbonatites, but despite this, many aspects of their origins and evolution remain obscure. Nevertheless, they are currently receiving enhanced attention among researchers because of their role in the deep time and deep Earth carbon cycle as well as their association with resources of Nb and rare earth elements (REE) and some other important commodities such as Fe, Cu, P, F, Ta, and U (Fortier et al. 2019, Løvik et al. 2018).

Here we review current understanding of the petrogenesis of carbonatite systems, using constraints from field observations, the petrology of natural samples and experimental analogs, as well as geochemistry. We begin with a discussion of the definition and classification of carbonatites.

2. WHAT ARE CARBONATITES?

2.1. A New Classification Scheme for Carbonatite Systems

Most rock classification schemes fit into one of two categories: descriptive or genetic. Descriptive classifications are based solely on observable characteristics of the rock type in question, most commonly mineral proportions or chemical compositions. They require no assumptions about the rock's origin or evolution.

The descriptive classification approach is currently used for carbonatites, employing the carbonate mineral contents of rocks that can be confidently interpreted to be igneous in origin. The required threshold volume percentage of carbonate minerals for a rock to be called a carbonatite has varied from greater than 70% (Kresten 1983) to greater than 50% (Streckeisen 1980) to greater than 30% (Mitchell 2005), with an upper limit of the silicate content set at 20% (Le Maitre 2002), further subdividing silica-rich rocks as silicocarbonatites. Several different varieties have been recognized, depending on the dominant carbonate mineral. These include calcite carbonatites (formerly referred to as sövite if coarse grained or alvikite if fine grained), dolomite carbonatite (formerly beforsite or rauhaugite), ferrocarbonatite (mainly Fe-carbonate minerals such as siderite or ankerite), and natrocarnatite (composed mainly of the alkali-dominated carbonate minerals nyerereite and gregoryite).

Chemically, carbonatites are descriptively classified into calciocarbonatite, magnesiocarbonatite, ferruginous calciocarbonatite, and ferrocarbonatite, which closely correspond to or replicate the mineralogical names calcite carbonatite, dolomite carbonatite, siderite calcite carbonatite, and ferrocarbonatite, respectively (Gittins & Harmer 1997, Woolley & Kempe 1989). Natrocarnatite is a further variety, rich in the chemical components Na_2CO_3 and K_2CO_3 relative to $CaCO_3$,

and known from the only currently active carbonatite volcano on Earth, Oldoinyo Lengai in Tanzania.

Mitchell (2005) argued persuasively that the lithological complexity of carbonatite complexes makes this purely descriptive definition inadequate. Because of magmatic differentiation¹ that invariably occurs in carbonatites emplaced into the crust, including fractional crystallization and formation of cumulates, modal mineralogy² can vary significantly over short length scales in the field. For example, an apatite + magnetite-rich cumulate spatially and genetically associated with a calciocarbonatite may not qualify as a carbonatite in the International Union of Geological Sciences definition (Le Maitre 2002, Streckeisen 1980). Mitchell (2005) suggested a mineralogical-genetic classification whereby an igneous rock containing greater than 30 vol% carbonate minerals is a carbonatite. Although this cutoff is arbitrary, it would allow classification as carbonatites of most of the range of modified rocks associated with carbonatite complexes. In most cases, “*a given carbonatite complex can be considered as a package of rocks that are modally diverse, but that have a common magmatic origin*” [Mitchell 2005, p. 2051 (italics in original)]. Additional mineral names can be added to the dominant carbonate phase—for example, apatite magnetite calciocarbonatite, etc.

Although empirical classification schemes are straightforward to use, they convey little information beyond a narrow scope of what the rock looks like and what minerals it contains. However, the key scientific questions relate to the origin and evolution of carbonatites: How did this rock form, why is it here, and what does it mean? Once scientific understanding of a rock-forming system is sufficiently advanced, a genetic classification scheme that takes into account the petrogenesis becomes possible. For example, granites are commonly classified into I, S, and A types because these categories relate to magma genesis. Whether a certain granitoid rock is lacking 1% of alkali feldspar and is therefore a granodiorite is inconsequential. Likewise, whether a carbonatite has 21% silicates or only 49% calcite is inconsequential. Carbonatite mineralogy often changes postemplacement. For example, an ankerite-dominated ferrocarbonatite can undergo near-surface oxidation in which ankerite is altered to calcite + hematite, changing the mineralogical ferrocarbonatite to a hematite calcite carbonatite, but the chemical ferrocarbonatite nature remains (Gittins & Harmer 1997). A genetic classification avoids such conundrums.

Current knowledge of carbonatite systems based on decades of study of natural occurrences, supplemented with extensive high-pressure experimental work, is sufficiently advanced to devise genetic definitions.

2.2. A Definition for Carbonatite Melts

A carbonatite melt is the crucial component underpinning the formation of any carbonatite system. At crustal pressures, carbonatite melts are clearly distinguished from silicate melts by their low silica contents. At mantle pressures, we only consider carbonatite melts as liquids that are broadly chemically equivalent to crustal carbonatite melts. Therefore, strongly carbonated silicate liquids such as kimberlites and ultramafic lamprophyres are not included in this definition, even if the carbonate anion may predominate at some stage during their petrogenesis. Nonetheless, carbonatite melts can coexist immiscibly with carbonated silicate melts. The most abundant cations in carbonatite melts are Ca^{2+} , Mg^{2+} , Fe^{2+} , Na^+ , and K^+ , and they often contain substantial phosphate, fluoride, chloride, and water in solution. Carbonatite melt compositions are rather

Carbonatite melt:
any high-temperature liquid in which carbonate predominates over all other anions combined and that solidifies into a mostly volume-filling mineral assemblage

¹Magmatic differentiation refers to the range of processes by which bulk magma chemical compositions are changed during emplacement into or eruption onto the crust, including crystallization of minerals.

²Modal mineralogy refers to the volume percent of different mineral types in a rock and is often the basis of mineralogical rock classification schemes.

enigmatic because they are not preserved in the geological record. Instead, they are inferred from melt inclusions and experimental studies.

Synmagmatic fluid:

any fluid phase that coexists in chemical equilibrium with a denser carbonatite melt

Brine-melt:

an H₂O-rich evolved carbonatite melt that lost most of its initial CaCO₃ and is now saturated with alkali- or Fe-rich carbonates

Paramagmatic fluid:

any fluid phase that is in chemical disequilibrium with a contemporaneous denser carbonatite melt

Postmagmatic fluid:

any fluid phase that interacts with a fully solidified carbonatite system and does not contain synmagmatic or paramagmatic components

Carbonatite rock:

any rock containing calcite, dolomite, ankerite, magnesite, siderite, or alkali carbonates that has crystallized from the melts described above

2.3. Fluids Associated with Carbonatite Systems

Carbonatite melts can occasionally be accompanied by synmagmatic fluids. These fluids span a wide range from H₂O-rich to H₂O-poor compositions, and they can contain CO₂ either in the gas phase or as carbonate, are often alkali rich, and are accompanied by a variety of anions such as chloride, fluoride, or sulfate.

Melt and fluid phases in carbonatite systems persist to temperatures lower than the solidi of other systems such as silicate magmas. Carbonatite melts continuously evolve by fractionating calcite, apatite, and dolomite, leading to concentration of other incompatible components such as alkalis, halides, and sulfate $\pm$ H₂O. These evolved carbonatite melts or brine-melts are highly distinctive from their parental carbonatite melts as they are in equilibrium with alkali carbonates that would otherwise dissolve in more dilute hydrothermal fluids.

Paramagmatic fluids often represent synmagmatic fluids that either (*a*) have been modified and often diluted by mixing with noncarbonatitic fluids or (*b*) have moved away and evolved distally to the location that contains its equilibrium carbonatite melt and mineral assemblage. For example, a relatively alkali- and Fe-poor synmagmatic fluid may form in a deeper section of the carbonatite system and rise toward a zone where an evolved brine-melt is actively crystallizing ankerite and carbocernaite. The fluid is now paramagmatic and can potentially destabilize ankerite and carbocernaite, mix with and modify the brine-melt, and cause autometasomatism of earlier formed solid assemblages. Once the magmatic and associated fluid activity of the carbonatite system has ceased, postmagmatic fluids can infiltrate the carbonatite. Postmagmatic fluids are externally derived, and their composition is buffered by the surrounding predominantly silicate rocks. Therefore, postmagmatic fluids are far from equilibrium with the unique chemical composition of carbonatite systems, and they often lead to substantial overprinting of the original mineral assemblages.

2.4. Carbonatite Rock Classification

The primary solid component of a carbonatite system is a carbonatite rock. The predominant crystallizing mineral during rock formation should be used as a prefix, excluding any obvious subsolidus modifications. For example, calcite that has exsolved dolomite lamellae should be considered purely as calcite, and ankerite that has exsolved iron oxides should be considered purely as ankerite. Other noncarbonate minerals of interest can be added as prefixes—for example, magnetite dolomite carbonatite or apatite calcite carbonatite. We discourage use of more than one noncarbonate mineral in the rock name—rock names should be short and simple. The mineral and bulk compositions of carbonatite rocks are not equivalent to the carbonatite melts from which the rocks crystallized. For example, calcite carbonatite did not necessarily crystallize from a calciocarbonatite melt. Note that our definition differs from the chemical classification of Le Maitre (2002), which uses oxide contents.

Carbonatite rocks can also contain various noncarbonate minerals such as wollastonite, magnetite, apatite, biotite/phlogopite, or forsterite so that when their oxide components (e.g., CaO, FeO + Fe₂O₃, P₂O₅, Al₂O₃, K₂O, and MgO) are included it may spuriously shift a chemical classification to an unrepresentative carbonatite type. For example, a carbonatite rock containing little calcite but abundant olivine should be called olivine calcite carbonatite in a genetic classification, although it may be chemically classified as a magnesiocarbonatite in descriptive schemes, falsely implying the presence of dolomite.

2.5. Fenites and Antiskarns

Carbonatite systems also include the products of metasomatic interactions between melts or fluids and the country rocks into which they intrude. The most commonly observed metasomatic silicate rocks are fenites. Fenites form by reactions between alkaline carbonatite-derived fluids and the surrounding silicate country rocks. Whether the fenitizing agents are carbonatite melts, evolved brine-melts, synmagmatic fluids, paramagmatic fluids, or a combination thereof varies greatly from one carbonatite system to the next. Fenites are characterized by the formation of metasomatic alkali-rich minerals such as micas, albite, K-feldspar, aegirine, and alkali amphiboles (arfvedsonite and riebeckite). Fenite bodies span a large size range, with some appearing as centimeter-scale selvages around carbonatite rocks while others extend several kilometers into the country rocks. Note that these alkali-rich minerals also occur in the igneous silicate rocks that are commonly associated with carbonatites, such as syenites, ijolites, and nephelinites. Thus, distinguishing real fenites from pristine alkaline silicate rocks that form part of a carbonatite complex may provide a challenge. These alkaline silicate rocks can themselves undergo fenitization by an adjacent carbonatite, leading to cryptic metasomatism that may create additional compositional complexity.

Other commonly observed metasomatic features in carbonatite systems are antiskarns. These zones record the influence or ingress of chemical components from the surrounding silicate rocks. These components react with the carbonatite melts, leading to mineral nucleation and growth within the magmatic conduit including its walls. Antiskarns—reaction products of carbonatite melt and solid host silicates—are essentially the opposite of classical skarns, in which carbonate-rich rocks such as limestones react with intruding silicate melts or associated fluids. Antiskarns typically contain Ca-Mg-silicate minerals characteristic of true skarns such as wollastonite, diopside, vesuvianite, cuspidine, etc. Antiskarnification of alkali-rich carbonatite melts will often lead to mineral assemblages resembling fenites. Fenites are, however, external to the carbonatite intrusion, whereas antiskarns form within a carbonatite body. Antiskarns do not necessarily contain carbonate minerals (thus they are not carbonatite rocks *sensu stricto*): The carbonatite melt can migrate away from the reaction site, leaving behind silicate-dominated rocks. (See the sidebar titled Anatectic Carbonatites and the sidebar titled Phoscorites.)

Fenite: alkali-rich metasomatic silicate rocks that form an aureole to an intrusive body of carbonatite rock

Antiskarn: a zone within a carbonatite intrusion containing a mineral assemblage that formed by contamination of a carbonatite melt with externally derived silicate material

ANATECTIC CARBONATITES

This review focuses on carbonatites that originate from carbonated alkaline silicate melts formed at mantle depths. However, this is not the only way to form natural carbonatite melts. Experimental work shows that partial melting of calcite and dolomite is feasible at upper crustal pressures and temperatures as low as 650°C, if sufficient H₂O is present (Durand et al. 2015, Lee et al. 2000). These conditions are not unusual in contact or high-grade regional metamorphic environments. Partial melting can be enhanced by infiltration of metamorphic fluids (Evans & Tomkins 2020) or hydrothermal brines expelled from nearby silicate intrusions (Audétat & Edmonds 2020). Whereas calcite and dolomite in mantle-derived carbonatite rocks represent the cumulates from alkali- and halogen-rich carbonatite melts, the rock compositions of anatectic carbonatites closely approximate those of melts. The mineral assemblages and geochemical signatures of anatectic carbonatites resemble those of marbles and their limestone or dolostone protoliths. Therefore, establishing that partial melting has occurred may not be straightforward, particularly if melt migration was limited so that the anatectic carbonatite melts did not escape from the (meta)sedimentary source rocks. Schumann et al. (2019) and Özkan et al. (2021) provide two examples for the presence of anatectic carbonatites, but there also exist cases where marbles with associated anatectic units have been debated as true mantle-derived carbonatites (cf. Hegner et al. 2020).

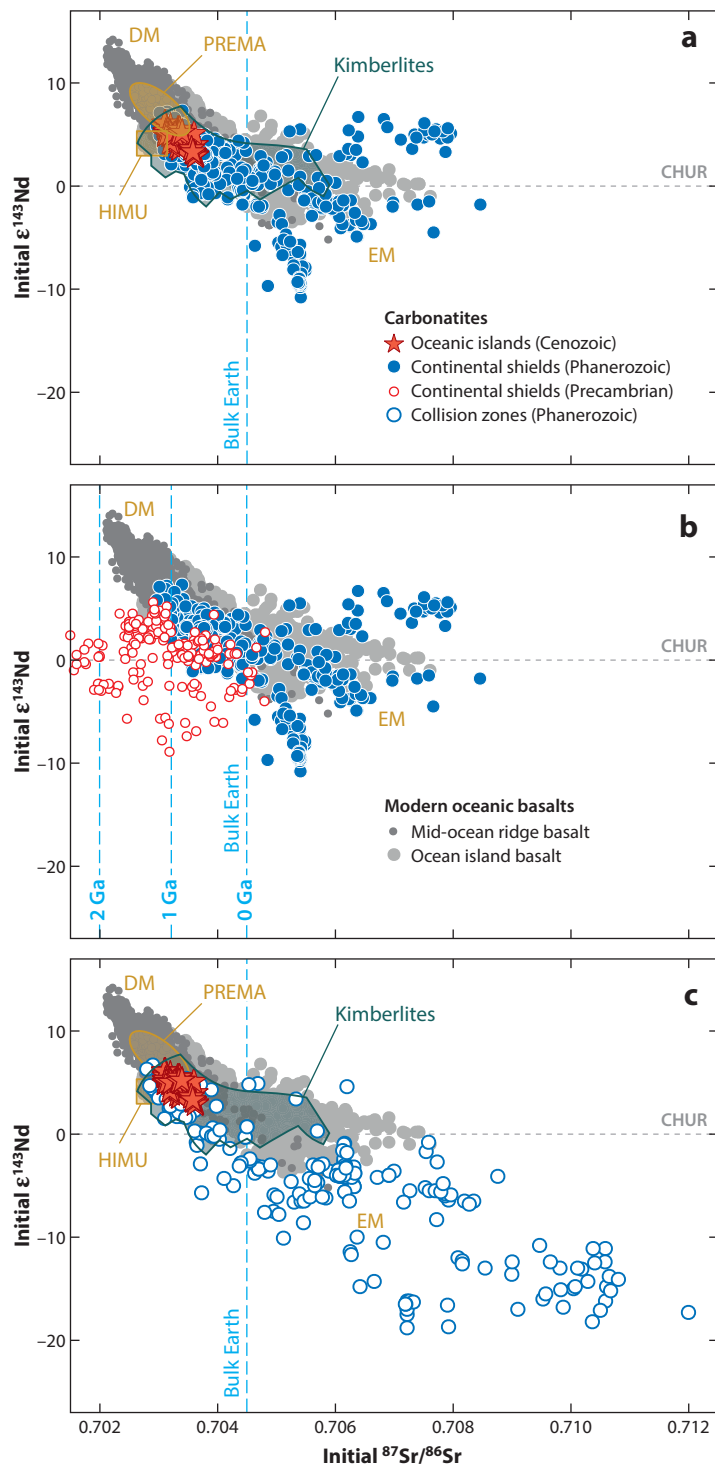
PHOSCORITES

Phoscorites are rocks containing varying proportions of apatite, magnetite, and Mg-dominated silicates (mostly olivine but also clinopyroxene and phlogopite). They are occasionally found in association with carbonatites and have diverse geometrical forms. While phoscorites are accepted to have originated from the same mantle source as their associated carbonatites, the petrogenetic relationships are even less clear compared to other rock associations of carbonatite systems (Giebel et al. 2019, Rass et al. 2020). Formation of phoscorites is a contentious subject with the two leading models suggesting either cumulates from fractional crystallization from carbonatite melts or phoscorite-carbonatite liquid immiscibility. Experiments by Klemme (2010) indicate that an Fe-P-rich melt can crystallize a phoscorite mineral assemblage with the residual liquid resembling carbonatite melts, supporting the fractional crystallization model. However, this model does not explain how an Fe-P-rich melt forms in the first place. Even the most recent studies on natural phoscorites are inconclusive, with some suggesting fractionation (Milani et al. 2017, Prokopyev et al. 2021), immiscibility (Giebel et al. 2019, Rass et al. 2020), or both (Barbosa et al. 2020).

3. ISOTOPIC EVIDENCE FOR THE MANTLE ORIGINS AND SOURCES OF CARBONATITES

Low-degree partial melting of Earth's upper mantle in the presence of CO₂-bearing fluids or carbonate minerals (dolomite, magnesite) has long been the dominant paradigm to explain carbonate-rich and associated alkaline silicate magmatism (Dalton & Presnall 1998, Eggler 1989, Lee & Wyllie 1998, Woolley & Kjarsgaard 2008, Yaxley et al. 2020). Recognition of carbonatite rocks as crystallization products of mantle-derived magmas led to numerous investigations that explored the space-time evolution of their source regions by means of radiogenic isotope analyses (Bell & Blenkinsop 1987, Nelson et al. 1988, Tilton & Bell 1994). This work established relatively uniform time-integrated evolutions for the Sr and Nd isotopic compositions of carbonatites from continental shields since the Late Archean (Bell & Blenkinsop 1987), which was ascribed initially to a common magma origin from depleted lithospheric mantle sources but was reinterpreted as a record of the isotopic evolution of the convecting mantle (Bell & Tilton 2002). Over the past 20 years, the isotope database for global carbonatites has grown exponentially (**Figures 1–3 and Supplemental Data**). This also includes nontraditional stable isotope systems such as ⁷Li/⁶Li, ²⁶Mg/²⁴Mg, and ⁴⁴Ca/⁴²Ca, which are increasingly explored to constrain the origins of carbonatites and the evolution of their mantle sources (e.g., Halama et al. 2008, Li et al. 2016, Sun et al. 2021, Tappe et al. 2017). The ever-growing isotope data sets are principally used to address the long-standing question of whether carbonatite magmas are derived from lithospheric or asthenospheric mantle sources and to evaluate the potential role of deeply sourced mantle plumes in their origin (Bell & Simonetti 2010). Another central question is whether anomalously strong geochemical enrichment is essential for preconditioning the mantle sources of carbonatites and, if so, whether the enrichment is driven internally involving primordial volatiles or driven mainly by recycled crust components within Earth's mantle (Amsellem et al. 2020, Horton 2021, Hulett et al. 2016, Hutchison et al. 2019, Tappe et al. 2017).

Early Sr-Nd-Pb isotope studies observed the similarity between carbonatites and ocean island basalts (OIBs), and it was suggested that the majority of Mesozoic–Cenozoic carbonatites were derived from relatively undepleted mantle sources dominated by high- μ end-member where $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$ and enriched mantle components (Bell & Tilton 2001, 2002; Nelson et al. 1988).



(Caption appears on following page)

Figure 1 (*Figure appears on preceding page*)

Variations of Sr and Nd isotopic compositions for global carbonatites as compiled during this study.

(a) Sr-Nd isotope data with a focus on carbonatites from modern oceanic islands and Phanerozoic carbonatites from continental shield settings. The compositional field for Group-1 kimberlites from cratons worldwide is based on the groundmass perovskite data compiled by Tappe et al. (2017). The data for modern oceanic basalts (mid-ocean ridge basalts and ocean island basalts) defining the mantle array are from Stracke (2012). (b) Sr-Nd isotope data with a focus on Phanerozoic and Precambrian carbonatites from continental shield settings. The Sr isotopic compositions of bulk Earth at 2 Ga, 1 Ga, and the present follow the Basaltic Achondrite Best Initial model. (c) Sr-Nd isotope data with a focus on Phanerozoic carbonatites from continental collision zone settings. CHUR calculated using the recommended average Nd isotopic composition of chondritic meteorites by Bouvier et al. (2008). DM, PREMA, HIMU, and EM calculated from Zindler & Hart (1986) and Stracke (2012). See the **Supplemental Data** for the data in this plot. Abbreviations: CHUR, chondritic uniform reservoir; DM, depleted mantle; EM, enriched mantle; HIMU, high- μ end-member where $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$; PREMA, prevalent mantle.

Supplemental Material >

Although an updated global database confirms the broad overlap between OIBs and young carbonatites from continental shield settings in Sr-Nd isotope space, the carbonatite data array develops between a well-defined moderately depleted end-member, similar to the prevalent mantle component of Zindler & Hart (1986), and a range of enriched isotopic components (**Figure 1a**). The isotopically enriched components are highly heterogeneous and have been variably interpreted as representing metasomatized continental mantle lithosphere (e.g., Bell & Simonetti 2010) or various types of recycled sediment (e.g., Chen et al. 2016, Hoernle et al. 2002), located either within the convecting upper mantle or within rising lower mantle plumes. Given that the few known carbonatites from oceanic islands (apparently restricted to the Central Atlantic) do not show strong Sr-Nd isotopic enrichment (**Figure 1a**), it would appear that the continental mantle lithosphere is, to variable extents, involved in the petrogenesis of carbonate-rich magmas beneath thick continental shields. The updated Sr-Nd isotope database also suggests that Phanerozoic and Precambrian carbonatites from continental shield settings are derived from similar mantle sources that comprise mixtures of moderately depleted and enriched components relative to primitive mantle compositions (**Figure 1b**). Although Phanerozoic carbonatites in collision zone settings also record a moderately depleted mantle component similar to their counterparts from continental shields, these orogenic to postorogenic carbonatites may extend to extremely enriched Sr-Nd isotopic compositions not known from the global OIB record (**Figure 1c**). Such a strongly enriched isotopic flavor is currently best interpreted as a sedimentary carbonate component that is added to certain mantle-derived low-volume magmas at crustal or shallow upper mantle depths in active continental collision zones (Hou et al. 2006, Lustrino et al. 2020), without the stretching and efficient size reduction that leads to the dispersal of deeply subducted sediments within the convecting mantle (Stracke 2012).

The updated Nd isotope database for global carbonatites shows a time-integrated evolution from ca. 3 Ga to the present that closely follows a chondritic or primitive mantle evolution, with some notable excursions to more depleted and enriched ϵNd^3 values, which are most prominent in the carbonatite data subsets for continental shields and collision zones, respectively (**Figure 2a**). A similar temporal evolution is defined by the Hf isotopic compositions of carbonatites and carbonatite-hosted zircon and baddeleyite from localities worldwide, albeit on the basis of many fewer data compared to the Nd isotope evolution (**Figure 2b**). Taken at face value, the Nd and

³Epsilon Nd (ϵNd) expresses the deviation in parts per 10^4 of the Nd isotopic composition of igneous rocks at time t after their formation, from the evolution of the chondritic uniform reservoir (CHUR), which represents the earliest, unfractionated material from which the Solar System formed. It is defined as $\epsilon\text{Nd} = \{[({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{sample}[t]} / ({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{CHUR}[t]}] - 1\} \times 10^4$ (DePaolo & Wasserburg 1976).

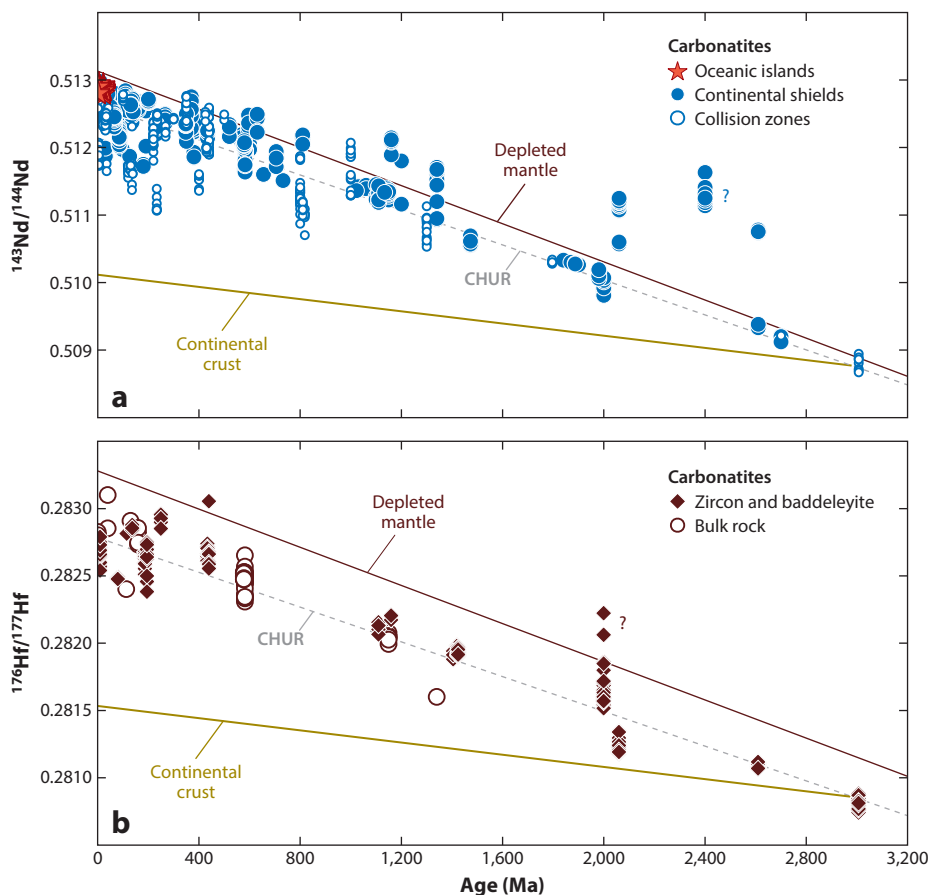
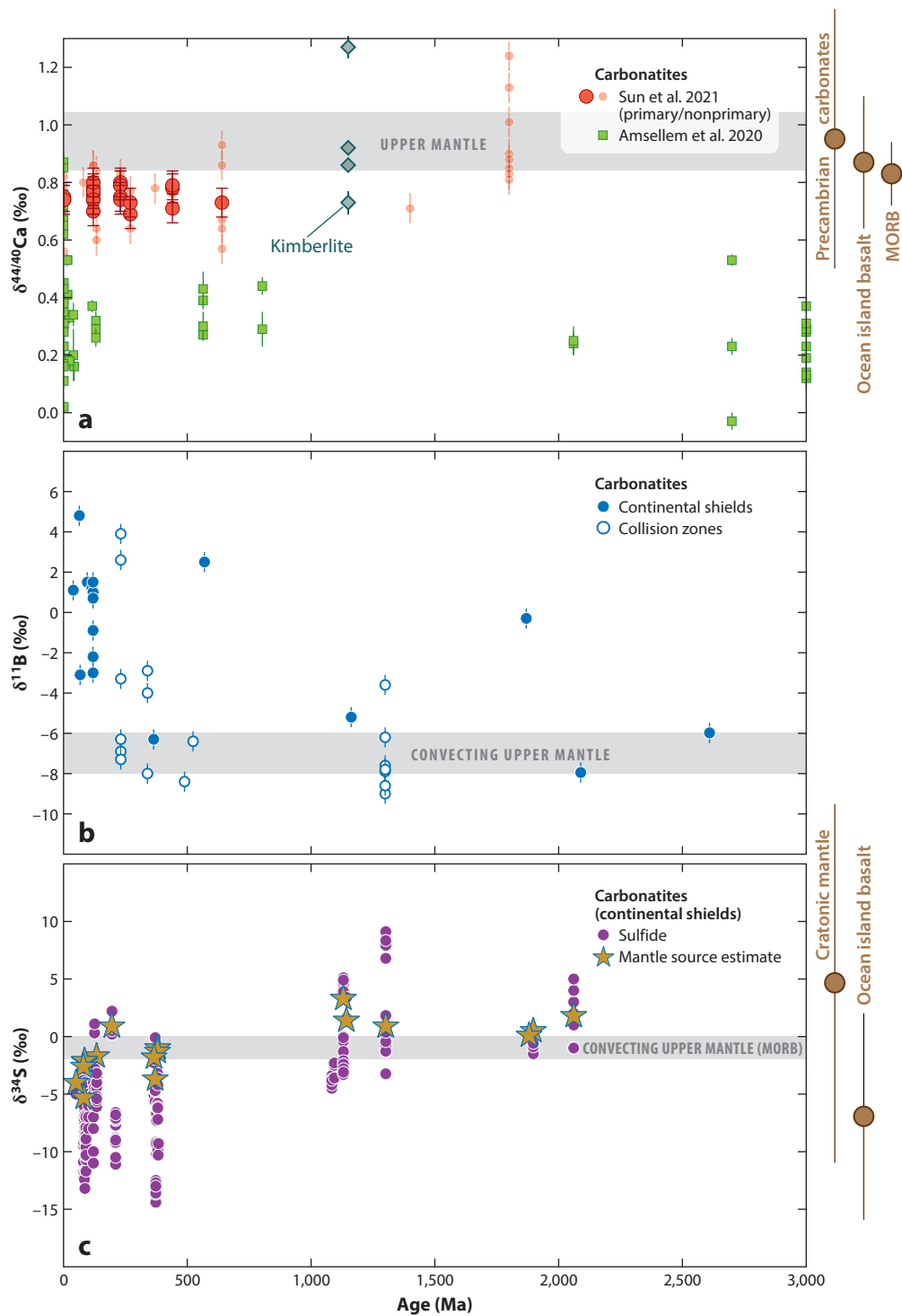


Figure 2

Evolution diagrams for the (a) Nd and (b) Hf isotopic compositions of global carbonatites as compiled during this study. Depleted mantle evolution follows the model by Salters & Stracke (2004). CHUR evolution uses the recommended average Nd and Hf isotopic compositions of chondritic meteorites and the respective parent-daughter element ratios, as given by Bouvier et al. (2008). Note the general paucity of Hf isotope data for bulk carbonatites due to the typically extremely low Hf concentrations, which presents a major analytical challenge. Abbreviation: CHUR, chondritic uniform reservoir.

Hf isotope evolution diagrams suggest an ultimate origin from the convecting upper mantle for global carbonatite magmatism through time (e.g., Bizimis et al. 2003, Tappe et al. 2020). However, the Nd and Hf isotope data compilations also suggest that recycled crustal components in the mantle sources of carbonatites became increasingly common after ca. 1 Ga (**Figure 2**), possibly due to the transitioning of Earth into a modern plate tectonics regime at lower geotherms during the Late Proterozoic (Hawkesworth et al. 2017). Establishment of colder subduction mechanisms with time may have promoted deeper levels of oceanic lithosphere transfer into the convecting mantle, including a more effective introduction of volatiles and sediments into the deep Earth (Thomson et al. 2016).

An important role for recycled marine carbonates in the mantle sources of global carbonatites has recently been suggested on the basis of extremely light Ca isotopic compositions (Amsellem et al. 2020) (**Figure 3a**). However, an improved analytical protocol revealed that



(Caption appears on following page)

Figure 3 (Figure appears on preceding page)

Evolution diagrams for the (a) calcium, (b) boron, and (c) sulfur stable isotopic compositions of global carbonatites, expressed in standard delta notations relative to the most widely used international reference materials. The main data sources are: for panel a, Amsellem et al. (2020), Sun et al. (2021), and Tappe et al. (2021); for panel b, Hulett et al. (2016) and Kuebler et al. (2020); and for panel c, Hutchison et al. (2019). Terrestrial mantle compositions follow the recommendations by Chen et al. (2016) for $\delta^{44/40}\text{Ca}$, Marschall et al. (2017) for $\delta^{11}\text{B}$, and Labidi et al. (2013) for $\delta^{34}\text{S}$. The $\delta^{34}\text{S}$ mantle source estimates for carbonatites from localities worldwide are taken from Hutchison et al. (2019). Abbreviation: MORB, mid-ocean ridge basalt.

most carbonatites have less extreme Ca isotopic compositions, more similar to those of oceanic basalts (Sun et al. 2021). Sun et al. (2021) argue that there is only a minor offset of carbonatite $\delta^{44/40}\text{Ca}$ values from the upper mantle range (**Figure 3a**) and that this systematic offset can be readily explained by melting-related isotope fractionation at ambient mantle temperatures. According to these authors' Ca isotope data, less than 2% of recycled carbonate sediments were involved in source-forming processes prior to mantle-derived carbonatite magmatism. While the evidence from Ca isotopes is currently inconclusive (**Figure 3a**), the fast-growing database of B and S isotope ratios in the most primitive carbonatites from localities worldwide suggests a secular evolution of their mantle source compositions (Amsellem et al. 2020, Hulett et al. 2016, Hutchison et al. 2019, Kuebler et al. 2020, Sun et al. 2021) (**Figure 3b,c**). Similar to the observation from the Nd and Hf isotope evolution (**Figure 2**), both the $\delta^{11}\text{B}$ (**Figure 3b**) and $\delta^{34}\text{S}$ (**Figure 3c**) values through time suggest marked contributions from recycled crustal components to global carbonatite magmatism during the Phanerozoic, whereas the data for Precambrian occurrences scatter around the respective mantle range.

4. PETROLOGICAL CONSTRAINTS ON THE FORMATION OF MELTS PARENTAL TO CARBONATITES

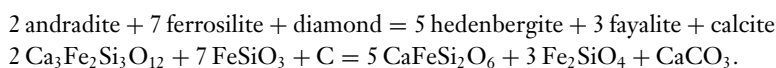
Given the isotopic evidence outlined in Section 3, that Phanerozoic carbonatites contain significant components derived from recycled crustal material, we now consider experimental constraints on the deep recycling of crustal carbon and its eventual incorporation into carbonatites.

The major process responsible for the return of crustal carbon to the deep mantle is subduction (Dasgupta & Hirschmann 2010, Kelemen & Manning 2015). Oceanic crust, hydrothermally altered in the ridge environment, typically contains a few percent of carbonate, mainly calcite (Alt et al. 1986, Hart & Staudigel 1978). Pelagic sediments can also be carbon rich (Plank & Langmuir 1998, Thomsen & Schmidt 2008). The fate of this material includes mass transfer as part of $\text{CO}_2 + \text{H}_2\text{O}$ -fluid to the serpentinized mantle wedge (the cold nose) in the forearc and storage as magnesite and other carbonates (Sieber et al. 2018, 2020), transfer into the subarc mantle wedge in fluids or melts (Poli et al. 2009), and eventual outgassing associated with arc or backarc volcanism or deeper subduction beyond the immediate arc environment (Kiseeva et al. 2013a, Thomson et al. 2016, Yaxley & Green 1994). More controversial is the relative magnitude of the fluxes of carbon in each case, and particularly how much carbon is subducted beyond the subarc environment, into the very deep mantle, and ultimately incorporated in the convecting mantle. Recent estimates vary from near-zero to 52 Mt C/a globally (Dasgupta & Hirschmann 2010, Kelemen & Manning 2015). The upper limit is comparable to estimates of the modern global CO_2 flux to the atmosphere from subduction-related volcanism (18–43 Mt C/a).

Isotopic evidence for recycled crustal components in Phanerozoic carbonatites suggests that the carbon flux via subduction to the convecting mantle has been greater than zero, at least during the past 1 Ga. Experimental studies have indicated that deeply subducted carbonate is likely to reach its solidus in mafic or sedimentary compositions modeling oceanic crust (Grassi & Schmidt 2011a,b, Kiseeva et al. 2013a, Thomsen & Schmidt 2008, Thomson et al. 2016) near or in the

mantle transition zone, along many feasible prograde pressure-temperature paths for subducting oceanic crust. Partial melts will be broadly alkali-rich calcic-magnesian compositions. They will undergo redox freezing on segregation from their recycled crustal sources and migration into peridotite wallrock. Peridotites present at depths corresponding to greater than or equal to 9 GPa are expected to be reduced (FeNi saturated, oxygen fugacity around the iron-wüstite buffer) (Ballhaus 1995, Frost & McCammon 2008). Reaction with carbonatite melts will initially form assemblages of diamond + Fe-Ni-S-carbide, depending on the abundance of carbon (Rohrbach et al. 2014, Tsuno & Dasgupta 2015). Further reaction will oxidize all Fe and Ni in carbides and produce hybrid, diamond-bearing pyroxenitic lithologies (Kiseeva et al. 2013b, Rohrbach & Schmidt 2011). If H₂O is present, methane fluids may form (Matjuschkin et al. 2018).

These diamond-bearing lithologies or methane-bearing fluids could then be entrained into the convecting mantle or in mantle plumes and decompressed. As they ascend, they will encounter progressively higher oxygen fugacity (Frost & McCammon 2008, Rohrbach & Schmidt 2011, Stagno et al. 2013), eventually permitting diamond and carbide oxidation to carbonate by oxygen exchange with Fe³⁺-bearing garnets and other mantle silicate minerals. One potential reaction involving the Fe-bearing components is



However, as shown by Dasgupta & Hirschmann (2006), it is unlikely that the convecting mantle could contain crystalline carbonate, as mantle adiabats with feasible potential temperatures [1,315–1,425°C (Ita & Stixrude 1992, McKenzie et al. 2005)] lie at temperatures well above the carbonate peridotite solidus. Based on experiments, these adiabats intersect this solidus at approximately 10 GPa, where conditions are likely much too reduced for carbonate stability. Instead, as a result of oxidation of the mantle during decompression, redox melting (Foley 2011) may occur at an oxidized peridotite solidus, producing alkali-bearing, calcic magnesian melt as the near-solidus liquid (e.g., Dasgupta & Hirschmann 2006, Falloon & Green 1989, Pintér et al. 2021). These melts would segregate and ascend at very low melt fractions (Hammouda & Laporte 2000, Kono et al. 2014) and evolve toward silica-undersaturated ultramafic to mafic silicate melts, similar to kimberlites, melilitites, and nephelinites, at lower pressures (Massuyeau et al. 2021).

The model process of deep recycling of carbon via subduction of crust and its eventual incorporation into mantle source regions for primary carbonatites or silica-undersaturated silicate melts is illustrated schematically in **Figure 4**.

Primary carbonatite melts may be produced near the peridotite + CO₂ ± H₂O solidus in the cooler lithosphere and will likely migrate along grain boundaries thermally buffered by the local geotherm. Emplacement directly into the crust may be hindered at pressures below 1.5–2.0 GPa by the carbonate limiting reaction dolomite + orthopyroxene = olivine + clinopyroxene + CO₂ [known as the carbonate ledge (Hammouda & Keshav 2015)], whereby carbonatite melt components will replace mantle orthopyroxene with olivine, clinopyroxene, and CO₂-rich fluid (Green & Wallace 1988). Evidence for this reaction has been recorded in some spinel peridotite xenoliths from Australia and Tanzania (Yaxley et al. 1991, Rudnick et al. 1993), in which replacement of orthopyroxene has in some samples been complete, leading to apatite-bearing wehrlites. Wehrlitization of melt conduits or channels, or rapid transport along deep lithospheric fractures, may allow subsequent primary dolomitic carbonatite melts to avoid reaction with orthopyroxene and elimination of the melt, so that emplacement at crustal levels as directly mantle-derived alkali-bearing calcic magnesian melts is possible (Dalton & Wood 1993).

However, about three-quarters of global carbonatite occurrences are spatially and temporally associated with silicate magmas (mainly nephelinites, melilitites, and syenites) in intraplate

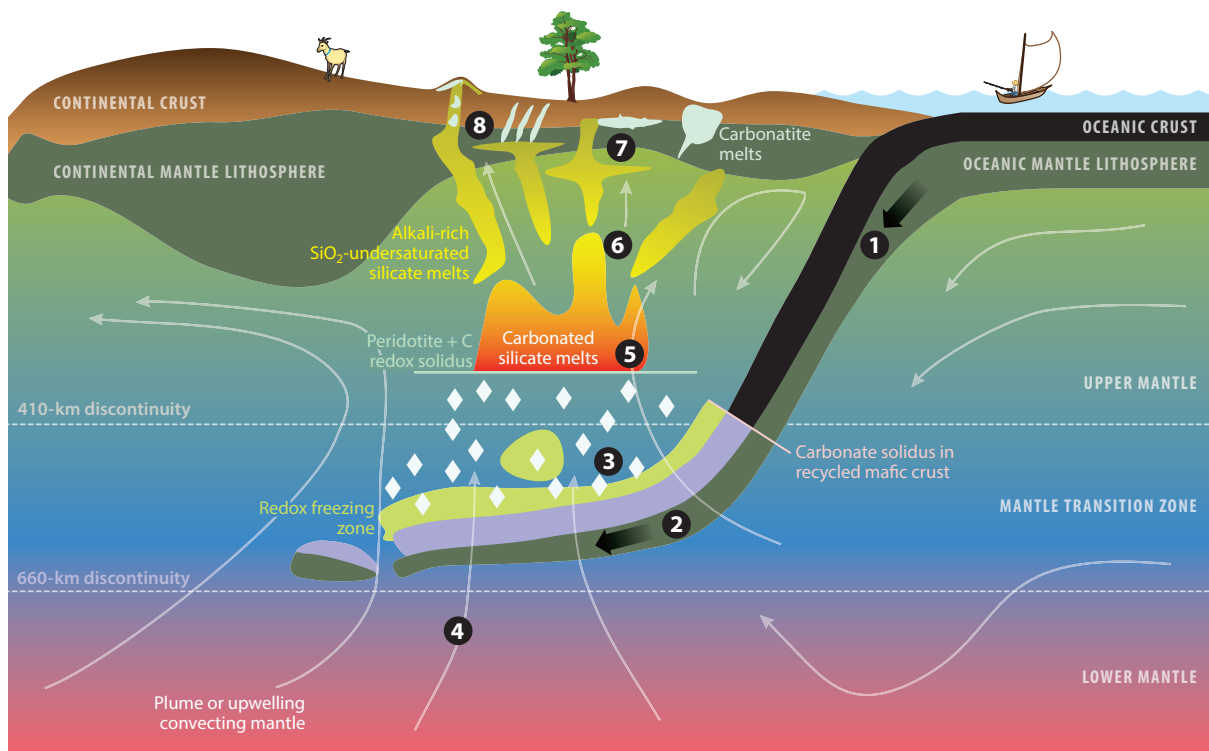


Figure 4

Schematic model for deep recycling of carbon leading to formation of carbonated undersaturated silicate melts in the mantle. Oceanic lithosphere is subducted, transporting hydrothermally introduced carbonate as part of the upper, mafic oceanic crust (❶). Some carbonate survives forearc and subarc processing and is subducted into the mantle transition zone (❷). Near the 410-km discontinuity, it crosses a carbonate eclogite solidus and produces carbonatite melts. These segregate and migrate into overlying peridotite wallrock, where the carbonate is reduced to diamond and FeNi carbides, a process known as redox freezing, which produces a hybrid, metasomatized zone of silicates, FeNi carbide, and diamond (❸). If H₂O is present, CH₄-rich fluids may be produced. Rising mantle plumes or upwelling convecting mantle, as illustrated by the thin light blue arrows, transport the reduced carbon zones upward (❹). As they decompress, they oxidize, eventually reaching a carbonate solidus and producing carbonated silicate melt (❺) by redox melting. This melt will segregate at very low melt fractions, move upward, and evolve toward CO₂-bearing undersaturated mafic to ultramafic silicate melts (❻). The melts will enter the lithospheric mantle and metasomatize it, or ascend toward the crust, where in some cases they may intersect a carbonate-silicate liquid solvus and produce carbonatite melt (❼), which may erupt (❽). Refer to **Figure 7** for more detailed information regarding crustal processes.

continental or in rare cases oceanic island settings. The carbonatites of these bimodal associations likely formed by silicate-carbonate liquid immiscibility after fractional crystallization of parental carbonated silicate melts. This probably happened in the crust or perhaps in the uppermost mantle lithosphere. Therefore, understanding the nature of crustally emplaced carbonatites' mantle sources and how and where they formed is closely linked to understanding how and where their parental silica-undersaturated silicate magmas formed.

The petrogenesis of intraplate basaltic rocks in continental and oceanic settings is controversial. There are competing models for their mantle source components, which include low melting temperature; metasomatically enriched and veined, volatile-bearing lithospheric mantle (e.g., Pilet et al. 2008, Rooney et al. 2017); or underlying asthenospheric mantle that has entrained a range of isotopically enriched components, some of which relate ultimately to recycled crustal materials incorporated into the convecting mantle via subduction. Melts derived from the asthenosphere

may also have metasomatized the overlying lithosphere, meaning that subsequent partial melts of the lithosphere contain geochemical signatures of components derived from the asthenosphere, or radiogenic isotope signatures grown in over geological time. In this case, it may be difficult to unravel the isotopic signatures of asthenospheric versus lithospheric melting. Direct asthenospheric melting may be initiated by adiabatic upwelling associated with mantle plumes, thinning of the lithosphere during rifting, or edge-driven convection (Davies & Rawlinson 2014). Alternatively, or in addition, thermal input from upwelling asthenosphere may have initiated melting in the volatile-enriched lithosphere.

The variations in primitive, silica-undersaturated magma compositions in continental or oceanic intraplate settings are a complex interplay of the depth and degree of mantle melting, the nature and abundance of volatile species present during partial melting ($\text{CO}_2 + \text{H}_2\text{O}$ particularly), and the nature of the sources involved (e.g., relative contributions by the asthenosphere and lithosphere). Nevertheless, formation of silica-undersaturated melts such as olivine-normative melilitite and nephelinite by partial melting of peridotite likely requires the presence of carbonate dissolved in the near-solidus liquid, due to its ability to contract the olivine liquidus field in the basalt tetrahedron relative to the volatile free system at high pressures, thereby moving low-degree partial melts into the nepheline-normative field. H_2O has the opposite effect, but a mixed $\text{CO}_2 + \text{H}_2\text{O}$ fluid dissolved in the primary silicate melt is still likely to lead to the formation of nepheline- or melilitite-normative compositions (Green et al. 1987). Olivine melilitites likely form in the presence of $\text{CO}_2 + \text{H}_2\text{O}$ -fluids in equilibrium with a garnet lherzolite residue at relatively high pressures (≥ 4 GPa) on a typical mantle adiabat at low degrees of melting ($< 1\%$). Olivine nephelinite likely forms at lower pressures and higher degrees of melting (≤ 3 GPa, 2%) (Brey 1978, Green 2015).

The next question relates to the conditions under which these silica-undersaturated melts can evolve by fractional crystallization to intersect a silicate-carbonate solvus and unmix into conjugate silicate and carbonatite melts.

5. CARBONATITE FORMATION BY CRYSTAL FRACTIONATION AND LIQUID IMMISCIBILITY

Experiments (Lee & Wyllie 1997, 1998) and melt inclusion records in early-formed minerals in Kovdor, Gardiner, Guli, and Kerimasi mafic silicate rocks associated with carbonatites (Guzmics et al. 2012, Nielsen et al. 1997, Rass & Plechov 2000, Veksler et al. 1998) and mafic-ultramafic alkaline silicate rocks associated with carbonatites (Frisch & Keusen 1977, Nielsen 1981, Panina & Motorina 2008, Ryabchikov & Kogarko 2016) suggest that at high temperatures ($\sim 1,050$ – $1,250^\circ\text{C}$) and crustal pressures (~ 0.1 – 1 GPa), crystallization of carbonated nephelinite-melilitite melts likely results in the formation of silicate (e.g., olivine, nepheline, clinopyroxene, melilitite, phlogopite, amphibole) and oxide (e.g., magnetite and perovskite) minerals. Such crystal fractionation⁴ causes compositional changes of the residual carbonated nephelinite-melilitite melts, sometimes leading to the formation of immiscible silicate and carbonatite melts (Brooker & Kjarsgaard 2011, Hamilton et al. 1979, Lee & Wyllie 1998, Schmidt & Wiedendorfer 2018) (Figure 5). Experimental and melt inclusion studies suggest that carbonatite melts forming at the onset of nephelinite-carbonatite immiscibility ($\sim 1,000$ – $1,100^\circ\text{C}$, ~ 0.1 – 1 GPa) are calcite

⁴Crystal fractionation is the most important process by which magma differentiation occurs. Crystals of mineral species precipitate from magmas and are physically separated from the remaining liquid, mainly because of density differences between the crystals and the melt, leading to chemical evolution of the magma.

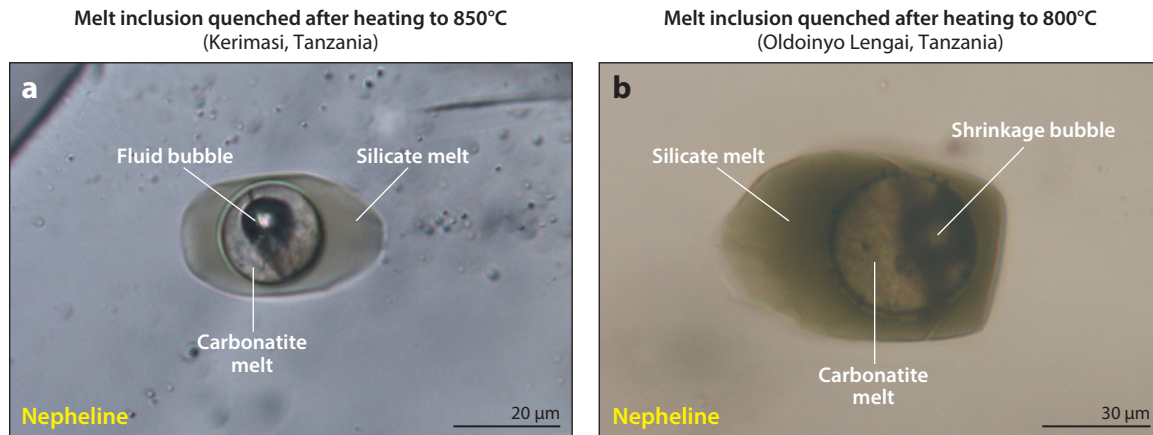


Figure 5

Melt inclusions hosted in nepheline crystals from Kerimasi (*a*) and Oldoinyo Lengai (*b*) in Tanzania. The inclusions were heated to 850 or 800°C and quenched, and they show evidence for immiscible silicate and carbonatite melts.

normative (30–45 wt% CaO), alkali (>7–10 wt% Na₂O + K₂O) and P₂O₅ bearing (2–7 wt%), and MgO poor (<3 wt%). Generally, immiscible carbonatite melts at 800–1,250°C are enriched in Na, K, Ca, Sr, Ba, light rare earth elements (LREE), P, Mo, W, F, and Cl relative to the coexisting silicate melts (Berkesi et al. 2020, Guzmics et al. 2015, Martin et al. 2012, Veksler et al. 2012). Some experiments suggest an alternative magma evolution path at crustal pressures, when initial carbonated nephelinite-melilitite melts can be CaCO₃ rich and coprecipitate silicates and calcite, without liquid immiscibility. This process may be recorded in silicate-calcite rocks found at Oka and Prairie Lake in Canada, and Kovdor and Belaya Zima in Russia (Doroshkevich et al. 2017, Savard & Mitchell 2021, Treiman & Essene 1985, Veksler et al. 1998).

Whether a particular primitive alkaline or tholeiitic basaltic melt can evolve by fractional crystallization in such a way that it intersects a carbonate-silicate liquid solvus depends on several factors. Schmidt & Weidendorfer (2018) showed that primitive basalts and basanites from 17 oceanic islands evolved toward high SiO₂ and Na₂O + K₂O contents, producing a broad array of compositions from basaltic andesites and trachyandesites to trachytes. However, for oceanic islands with recorded carbonatites (Cape Verde and the Canary Islands), primitive basanites have lower SiO₂ and higher total alkalis, with fractionation toward phonolites. Both arrays terminate at a valley on the liquidus surface of the KAlSiO₄-NaAlSiO₄-SiO₂ system (Zeng & MacKenzie 1984). This valley has a phonolite minimum at very high total alkalis (18 wt% Na₂O + K₂O) at around 52–56 wt% SiO₂ and a granite minimum at around 9 wt% Na₂O + K₂O and 72–76 wt% SiO₂. In between the two minima is the alkali feldspar thermal divide (13–14 wt% Na₂O + K₂O, 64 wt% SiO₂). The maximum extent of the experimentally determined silicate-carbonate solvus intersects the cotectic near the phonolite minimum (see the supplementary information of Schmidt & Weidendorfer 2018). This means that primitive carbonate-bearing silicate melts that evolve toward highly alkaline, broadly phonolitic compositions may intersect the carbonate-silicate solvus and produce conjugate immiscible carbonatite and silicate liquids. Melts evolving toward the lower total alkali-high SiO₂ side of the thermal divide will potentially terminate at the granite minimum and never exsolve a carbonatite liquid. The rarity of oceanic carbonatites may relate to low CO₂ solubility in evolved melts at relatively shallow crustal pressures, whereas fractionation in the deep continental lithosphere tends to promote high CO₂ solubility and thus the potential to form discrete quantities of carbonatite melt that can intrude the crust or erupt at Earth's surface. This

concept is supported by the fact that those oceanic islands with known carbonatites have some of the thickest lithospheres within the ocean basins (Schmidt & Weidendorfer 2018).

6. EARLY EVOLUTION AND EMPLACEMENT OF CARBONATITE MAGMAS

Once carbonatite melts are emplaced into the crust, regardless of whether they came directly from the mantle or evolved by liquid immiscibility, they will be rich in the CaCO_3 component. In addition, they contain alkalis (mainly Na and K), some Mg, and both Fe^{2+} and Fe^{3+} . Anionic species in the melt include abundant phosphate, fluoride, chloride, and sulfate. These initial carbonatite melts will evolve via fractionation of calcite $\pm$ apatite forming calcite carbonatite rocks (Guzmics et al. 2011, Weidendorfer et al. 2017) or by a decarbonation reaction between the CaCO_3 component in the melt with silica sourced from the surrounding wallrocks, leading to formation of wollastonite antiskarns. Magnesium will also participate in the decarbonation reaction forming clinopyroxene antiskarns and potentially olivine in Mg-rich carbonatite melts or adjacent to ultramafic wallrocks (Anenburg & Mavrogenes 2018). During these early stages of carbonatite evolution in the crust, oxide minerals such as magnetite and perovskite frequently occur. Silicate minerals also crystallize, most commonly olivine, phlogopite, clinopyroxene with varying aegirine contents, and a range of amphibole compositions from Ca-Mg at early stages to alkali amphiboles later on (Anenburg et al. 2020a, Feng et al. 2020, Kjarsgaard 1998). The required SiO_2 and Al_2O_3 either can be sourced from the primitive carbonatite melt itself or was added to the evolving carbonatite liquids via wallrock assimilation (Anenburg & Mavrogenes 2018).

7. ARE DOLOMITE CARBONATITES DIRECT MANTLE MELTS?

Much has been argued about whether some carbonatites crystallized directly from carbonatite melts that formed in the mantle or whether they are products of differentiation of carbonated silicate melts, by liquid immiscibility and/or crystal fractionation. The common association of carbonatites with alkaline silicate rocks supports their derivation from carbonated silicate melts (e.g., Tappe et al. 2017). However, a few studies argued that the coexisting carbonatite and silicate rocks in some igneous complexes merely used the same crustal conduits but may have had distinct origins and are not petrogenetically related (Harmer 1999). Of importance in this debate are dolomite carbonatites, which are often considered to represent the crustal emplacement products of mantle-derived Mg-rich carbonatite melts (Harmer & Gittins 1997).

Figure 6 shows several decarbonation reactions in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$. These reactions relate to pure end-member components with unit activity, but they offer reasonable approximations for carbonatite melts and the relevant crystalline phases. Decarbonation reactions have a moderate slope in pressure-temperature space, but rising mantle melts are near adiabatic with steep initial slopes (gray arrow in **Figure 6**). As they rise, the melts encounter crustal rocks with higher SiO_2 and Al_2O_3 contents compared to mantle rocks at decreasing pressures. The carbonatite melts may react with silicate crustal minerals, consuming the melt's dolomite component (**Figure 6**) and leaving behind a Ca-enriched carbonatite melt. Such Ca-dominated carbonatite melts need abundant fluxing components to remain liquid and to reach the upper crust, and melt inclusion evidence indicates high concentrations of the alkalis, F, H_2O , etc. Without these fluxing agents, carbonatite melts may simply freeze in the lower or middle crust after having lost one of their most important fluxing components— MgCO_3 . These melts can be preserved as zones containing abundant clinopyroxene [i.e., antiskarns (e.g., Shaw 2018)] but are difficult to recognize in the absence of exposures of deep pyroxenites. The process described above is similar to

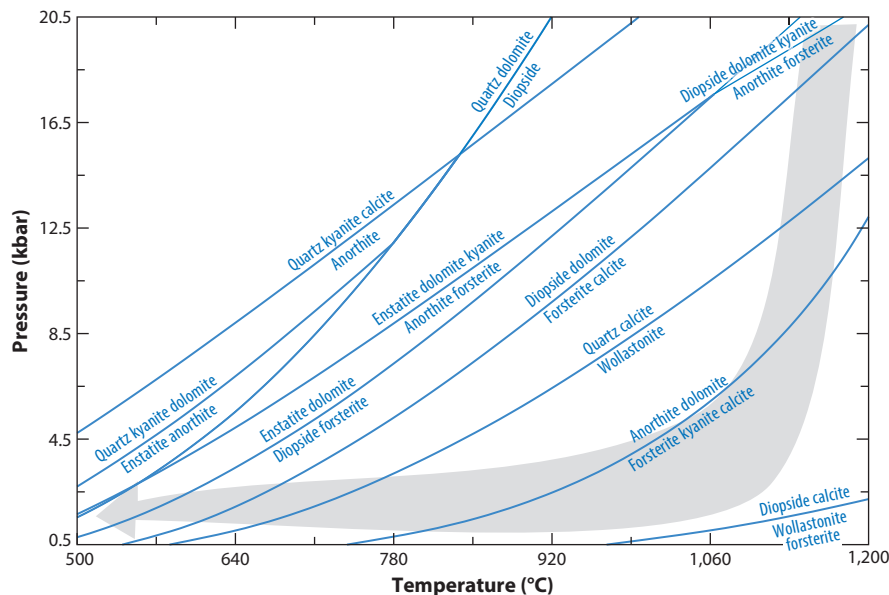


Figure 6

Silicate-carbonate reactions at crustal pressures, calculated using *Perple_X*. The gray arrow represents schematically the pressure-temperature path followed by an ascending carbonatite liquid, which is initially adiabatic (nearly vertical in pressure-temperature space) and then cools when it reaches its emplacement level in the crust.

the model by Hammouda et al. (2014), where a hot magnesian carbonatite melt bypasses the carbonate ledge and subsequently reacts with the lower crust to produce olivine and a more calcic carbonatite melt. We note, however, that this reaction is less likely to occur in the upper crust because olivine is not stable at these conditions. Regardless of the details of such reactions, it is important to recognize that rising mantle-derived carbonatite melts almost certainly lose a significant amount of their Mg to the encountered country rocks in Earth's crust. The formation of mantle wehrlite is often explained as a mechanism by which magnesian carbonatite melts can escape reactions at the carbonate ledge at shallow mantle depths and enter relatively unmodified into the crust (Dalton & Wood 1993).

Once in the upper crust, carbonatite melts will cool down and crystallize primarily calcite, enriching the residual melt in Mg and approaching the dolomite stability field. These evolved carbonatite melts will reach a stage when dolomite becomes the main crystallizing phase instead of calcite, resulting in the formation of dolomite carbonatite rocks. In essence, a mantle-derived carbonatite melt may lose most of its MgCO_3 component upon ascent but may subsequently be enriched in MgCO_3 during fractional crystallization in the uppermost crust.

Alternatively, a carbonatite melt formed by liquid immiscibility from a carbonated silicate melt will initially have a low Mg content but will evolve to higher MgCO_3 content due to calcite crystallization. Therefore, the presence of dolomite in a carbonatite rock may not relate directly to its mantle origin or differentiation via liquid immiscibility but can be controlled by magma evolution within the upper crust. Harmer & Gittins (1997, p. 5) argue that “no reasonable petrogenetic mechanism exists whereby magnesian carbonatite magmas could be generated from calcitic parental melts: it is argued that the reverse is true.” This statement assumes that calcite carbonatite rocks derive from Ca-dominated or calcitic melts and that dolomite carbonatite rocks derive from

Mg-dominated or dolomitic melts. Neither of these theoretical end-member melts is likely to exist in nature. Natural carbonatite melts are a solution of a wide range of chemical components, including Ca, Mg, Fe, Na, K, P, F, Cl, H₂O, and more. Whether calcite or dolomite or both mineral phases crystallize from such melts depends on their temperature evolution and the previous crystallization history. Contamination of ascending carbonatite melts by silicate mineral reactions and assimilation processes suppresses the crystallization of dolomite because Mg is preferentially incorporated into newly formed antiskarn materials containing silicates such as diopside, phlogopite, and amphibole (Anenburg et al. 2020a, Giebel et al. 2019, Wei et al. 2020). Therefore, calcite carbonatites, dolomite carbonatites, and mafic silicate calcite carbonatites can potentially all form from the same parental carbonatite magma, depending on the complex evolutionary paths taken by a primary magnesian carbonatite melt from the upper mantle or by a calcic carbonatite melt conjugate to an undersaturated silicate melt (Djeddi et al. 2021).

8. NATROCARBONATITES AND THEIR ABSENCE FROM THE GEOLOGICAL RECORD

Much controversy surrounds the formation of natrocarbonatite melts periodically erupting at Oldoinyo Lengai at ~500–600°C (Dawson et al. 1990, Keller & Krafft 1990). Experimental results (Sweeney 1994, Wallace & Green 1988) rule out that natrocarbonatites, containing less than 1 wt% MgO (Keller & Krafft 1990), represent melts that were derived directly from the mantle. Phase diagrams suggest that if immiscible nephelinite and carbonatite melts coexist from ~1,200 to 850°C, silicate (and oxide) minerals preferentially form and calcite precipitation is limited to a narrow compositional field (Kjarsgaard 1998; Lee & Wyllie 1997, 1998). This can be responsible for the formation of diverse nephelinite-phonolite and melilitite rocks (Mitchell 2005, Schmidt & Wiedendorfer 2018), containing minor or no calcite. Melt inclusion data suggest that at 800–850°C and subvolcanic pressures, the fluid phase can be volumetrically significant, silicate melt compositions can shift from mafic-intermediate nephelinitic to phonolitic, and carbonatite melts tend to have compositions that can produce nyerereite and are enriched in F (5–14 wt%) (Baudouin et al. 2018, Berkesi et al. 2020, Guzmics et al. 2019). Calcite saturation from these F-rich carbonatite melts is unlikely because fluorine suppresses the calcite liquidus (Jago & Gittins 1991). Melt inclusions in calcite carbonatite rocks from Guli in Russia and Oka in Canada show in addition alkali-rich compositions (Chen et al. 2013, Kogarko et al. 1991).

Natrocarbonatites at Oldoinyo Lengai consist of nyerereite and gregoryite phenocrysts set in a fluorite + sylvite-bearing groundmass, which is enriched in halogens (2–6 wt% F, 3–6 wt% Cl). These rare natrocarbonatites are associated with strongly peralkaline evolved nephelinites (Church & Jones 1995, Keller & Krafft 1990, Kjarsgaard et al. 1995, Peterson 1989). Melt inclusions from Oldoinyo Lengai reveal the coexistence of highly peralkaline, evolved nephelinite melts (de Moor et al. 2013, Sharygin et al. 2012) with immiscible gregoryite- or nyerereite-normative carbonatite melts (Mitchell 2009, Mitchell & Dawson 2012) at ~750–800°C (Berkesi et al. 2020) (**Figure 5**). The high peralkalinity of the nephelinite melts was explained by clinopyroxene dissolution in a CaCO₃-rich carbonatite melt (Weidendorfer et al. 2019) or by re-equilibration of a gregoryite-rich fluid residue (Guzmics et al. 2019) with immiscible phonolite and F-rich carbonatite melts after CO₂-rich vapor degassing (Berkesi et al. 2020). These F-rich gregoryite + nyerereite normative carbonatite melts can fractionate fluorite at less than 750°C, resulting in natrocarbonatite compositions alongside the complete solidification of the coexisting nephelinite melts.

An often-discussed enigma of carbonatite petrology is the lack of natrocarbonatites in the geological record, which is dominated by calcite- and dolomite-bearing varieties among the more

than 600 known carbonatite occurrences. This led to the hypothesis that natrocarbonatites have an exceptionally poor preservation potential because of their soluble alkali-rich nature (e.g., Martin et al. 2012). Alternatively, the recent Oldoinyo Lengai natrocarbonatites may present a geochemical anomaly. This debate could potentially be resolved if calcite and dolomite carbonatites are considered as cumulate crystallization products and the natrocarbonatite as the residual melt. An initially heterogeneous carbonatite melt will contain Ca, Mg, Na, and K. Given that calcite is the primary crystallizing phase followed by dolomite, these cumulates will form the carbonatite rocks (Slezak & Spandler 2020). The fractionated carbonatite melt will then be depleted in Ca and Mg, with strong enrichments of Na and K (Guzmics et al. 2011). Weidendorfer et al. (2017) demonstrated that an evolved carbonatite melt will consist of less than 50% CaCO_3 with the remainder comprising mostly Na_2CO_3 and K_2CO_3 , while still crystallizing solely calcite on the liquidus. Subsequent evolution to brine-melts by crystallization of dolomite and ankerite will further increase the Na-K to Ca-Mg ratio of the residual melt. Although melt inclusions thought to be associated with natrocarbonatite eruptions are H_2O poor (Berkési et al. 2020, Guzmics et al. 2019), they could have been degassed prior to entrapment. Eruptions at Oldoinyo Lengai are occasionally accompanied by abundant H_2O fluxes (Fischer et al. 2006, Teague et al. 2008), which could represent degassing of the aqueous brine component of the brine-melt, leaving behind a relatively dry natrocarbonatite. Alternatively, the H_2O component could be groundwater derived, or it could be generated by shallow CO_2 - H_2O phase separation.

Thus, calcite-dolomite carbonatites and natrocarbonatites are not mutually exclusive. They appear to represent the carbonatite cumulate and evolved carbonatite melt components of the same magmatic system. Most calcite and dolomite carbonatites emplaced as cumulates into the uppermost crust may have had an associated alkali carbonatite melt component. A natrocarbonatite may be the surface expression of an evolved carbonatite melt, similar to the condensate model by Nielsen & Veksler (2002). Had it not erupted, it would have been consumed in metasomatic reactions with silicate country rocks to form a fenite aureole (see Section 9). Given that most carbonatite complexes have a fenite aureole, it is reasonable to argue that natrocarbonatites have been common in the geological past and do not represent a modern geochemical anomaly. However, it remains unclear how common natrocarbonatite eruptions analogous to Oldoinyo Lengai were in the distant past.

Although soluble alkali minerals were formed experimentally (Anenburg et al. 2020b, Mitchell & Kjarsgaard 2011) and are common in fluid and melt inclusions (Chakhmouradian et al. 2016, Bühn & Rankin 1999), they probably did not form plutonic natrocarbonatite rocks but rather occur in segregations within dolomite and ankerite carbonatites, or are widely disseminated within them (Tucker et al. 2012). This implies that the Oldoinyo Lengai sodic lavas are not particularly unusual, despite the fact that most fossil carbonatites are alkali poor and calcite rich. The processes of immiscibility and fractional crystallization inferred for the Oldoinyo Lengai and Kerimasi volcanoes of the East African Rift System may be the standard petrological mechanism by which Na-poor calcite and dolomite carbonatites are produced, also in the geological past. Clearly, the natrocarbonatite lavas of Oldoinyo Lengai are unstable and difficult to preserve in the surficial environment because of the soluble nature of the sodic carbonate minerals. These lavas begin to react with the atmosphere within hours after eruption and are mostly dissolved within a few weeks, with the alkalis being transported to Lake Natron in the rift valley, which owes its extreme alkalinity to the ephemeral nature of natrocarbonatites. In summary, the extreme rarity of natrocarbonatite in the geological record likely relates to its loss from fractionally crystallizing carbonatite magma during fenitization; also, in situations where natrocarbonatite forms as a highly fractionated liquid during fractional crystallization of carbonatite magma and is erupted, it is lost due to the instability of Na-rich carbonate minerals in the surface environment.

9. FENITIZATION AND METASOMATIC REACTIONS WITHIN THE CRUST

One of the most notable features of carbonatite emplacement in the crust is fenitization. Although the concept of fenitization encompasses various definitions, it can be broadly described as a metasomatic process that leads to a loss of silica and gain in alkalis (notably Na) within the immediate country rocks into which a carbonatite magma intruded (e.g., Le Bas 2008, Woolley 1982). The extent of the fenitized zone and the intensity of metasomatic overprinting vary greatly between localities. They strongly depend on the chemistry of the fluids and host rocks, country rock permeability, duration of the metasomatic events, fluid/rock ratio, and geometry of the fluid channel system. Synmagmatic and paramagmatic fluid phases coexisting with carbonate or immiscible silicate-carbonatite melts are thought to be diverse (Walter et al. 2021), ranging in compositions from alkali-carbonate $\pm$ alkali-sulfate + CO_2 + H_2O (Guzmics et al. 2011, 2019; Nielsen & Veksler 2002, Rankin 1975, Veksler & Keppler 2000) to halite + H_2O + CO_2 (Bühn et al. 2002, Walter et al. 2020). Thus, alkali-rich fluids are expelled from cooling carbonatite and alkaline silicate magmas (e.g., Guzmics et al. 2019, Le Bas 2008), and they are the main driver of country rock fenitization (Cooper et al. 2016), which includes their ability to carry and remobilize the REE (Anenburg et al. 2020b, Bühn & Rankin 1999, Horton et al. 2021, Xu et al. 2010). Alternatively, fenitization may be driven by the action of the carbonatite melts or brine-melts themselves, without involvement of a separate fluid phase. An alternative source of the required alkalis is provided by alkali-rich carbonates such as nyerereite, gregoryite, eitelite, rouvilleite, and burbankite. These and similar minerals are unstable at geological timescales, and their breakdown would release alkalis available for fenitization (Zaitsev & Keller 2006).

Sodic fenites are typically found around intrusive carbonatite bodies and relate to high-temperature fluids, whereas potassic fenitization (i.e., the feldspathic fenite type) occurs preferentially at subvolcanic levels and is frequently associated with brecciation events (e.g., Le Bas 2008). The alkali contents of fluids depend on the depths of carbonatitic magma differentiation in connection with crystal fractionation and immiscibility processes (Woolley & Church 2005). Decoupling of Na-K may relate to the crystallization of sodic carbonates, which effectively fractionates Na from the most evolved brine-melts, whereas no potassic carbonates are known to form (Anenburg et al. 2020b). Most carbonatite and alkaline igneous complexes formed by repeated magmatic pulses, and thus, fenitization can be considered as a multistep process during which each pulse may develop a new discrete alkali-rich fluid (Decrée et al. 2020b).

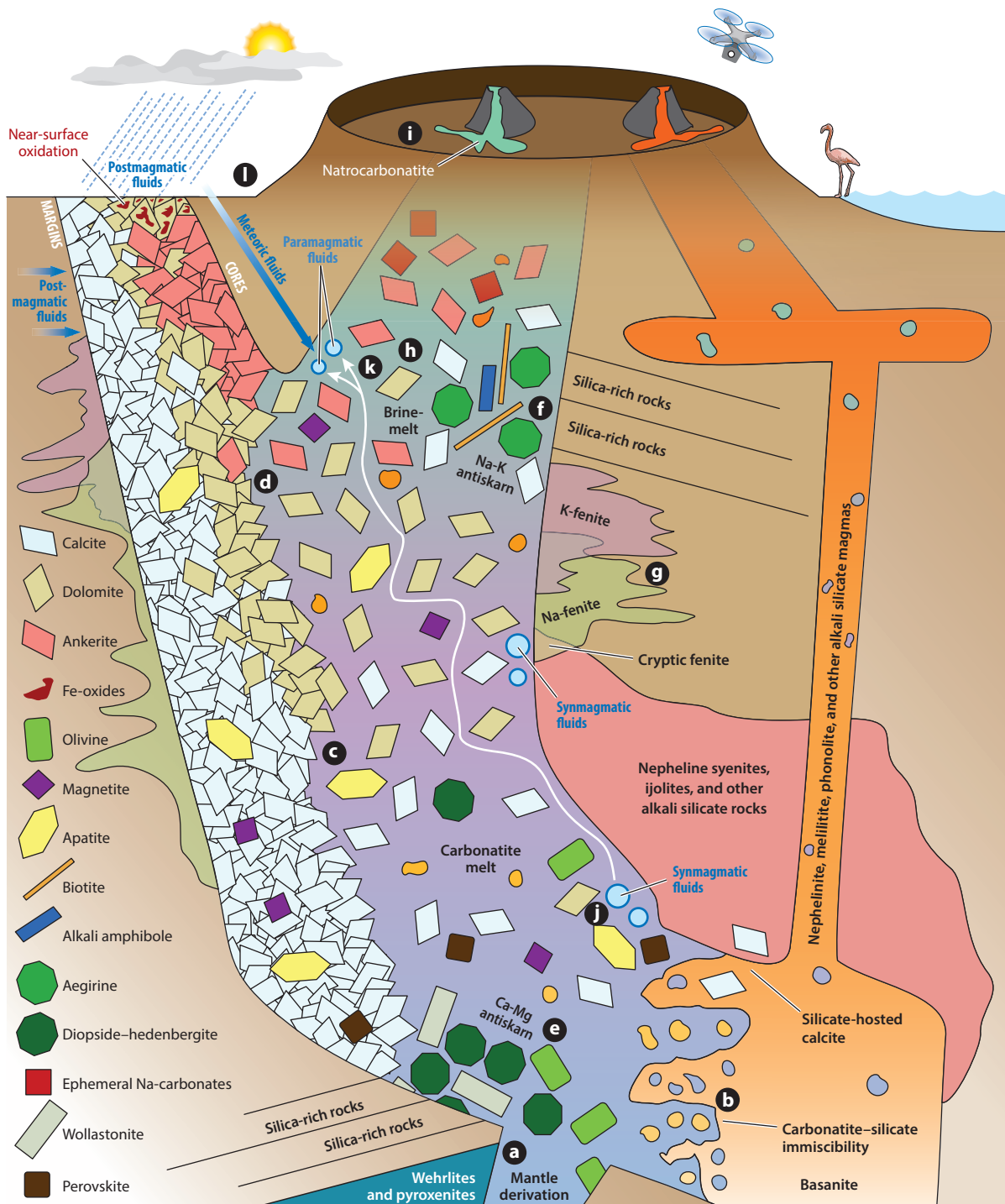
Hydrothermal fluids use and reuse the same plumbing system as the main carbonatite bodies, generally exploiting structural weaknesses. This typically leads to a superimposition of various magmatic and hydrothermal processes at the scale of a single carbonatite occurrence (e.g., Andersson et al. 2013, Pirajno 1994, Woolley & Kjarsgaard 2008). This is even more prominent in cases where shear zones controlled the emplacement of carbonatite magmas and influenced the geometry of the intrusive bodies. Major shear zones act as corridors for fluid flow and circulation, giving rise to successive metasomatic events by which the country rocks of carbonatite intrusions can be mineralogically altered (Decrée et al. 2015).

In **Figure 7**, we summarize the processes reviewed above, by which carbonatite melts can evolve in the uppermost mantle and crust.

10. ORE DEPOSIT FORMATION

10.1. Rare Earth Elements

Interpreting ore formation in carbonatites is often challenging because carbonatite rocks are invariably overprinted by paramagmatic and postmagmatic hydrothermal activity (e.g., Fosu



(Caption appears on following page)

Figure 7 (Figure appears on preceding page)

A schematic sketch illustrating an idealized carbonatite system. Carbonatite melts can come directly from the mantle (*a*), in which case they are likely to react with surrounding rocks to form wehrlites and pyroxenites. Alternatively, they can form by immiscibility with a silicate melt at crustal pressures (*b*). The first carbonate mineral crystallizing for most carbonatite melt composition is calcite (*c*), followed by dolomite with increasing ankerite contents (*d*). The color gradient in the carbonatite melt represents increasing Na, K, and Fe contents and decreasing Ca and Mg contents. When in contact with silica-rich rocks, the carbonatite melt could react to form antiskarns with compositions that primarily depend on the melt composition at that location (*e, f*). Note that the figure depicts an antiskarn while it is forming, and fossil antiskarns may not necessarily contain substantial carbonate minerals. Carbonatite melts may react with the surrounding wallrocks and metasomatize them into fenites (*g*). Sodic fenites tend to form deeper and earlier, whereas potassic fenites form shallower and later. One may overprint the other. Fenitization may be less obvious (cryptic) when it is affecting an alkali silicate rock. The most evolved carbonatite melts are typically highly enriched in Na and K and are referred to as natrocarbonatites. In cases where H₂O is strongly elevated and the melts resemble brines, they are referred to as brine-melts (*h*). Natrocarbonatite melts and brine-melts are in equilibrium with Na-rich alkali carbonates. Natrocarbonatite rocks have never been found in plutonic settings in nature due to their ephemeral nature, but they may reach the surface to form natrocarbonatite lava flows (*i*). Substantial degassing of H₂O would occur if the erupting melt were a brine-melt. Rapid ascent of deeper, less alkaline melts can cause brecciation and explosive carbonatite volcanism and formation of tuffs (not shown). Synmagmatic fluids exsolved from the carbonatite melt will be in equilibrium at the place of exsolution (*j*), but once they migrate to other parts of the carbonatite system, they will be out of equilibrium and become paramagmatic fluids, potentially mixing with externally derived fluids (*k*). Postmagmatic fluids are those fluids that operate once the carbonatite system is no longer active (*l*).

et al. 2021, Slezak & Spandler 2020, Ying et al. 2020). Carbonatites are renowned for their LREE deposits, as currently most if not all of the world's LREE and a substantial portion of heavy rare earth elements (HREE) are sourced from carbonatites and related rocks. Experimental evidence shows that carbonatite-associated REE mineralization is essentially magmatic and that the partitioning of REE to synmagmatic fluids is negligible (Song et al. 2016). Alkali carbonates such as burbankite and carbocearnite are the principal REE-dominated minerals crystallizing from brine-melts, which are the REE-enriched late-stage carbonatite melts. As the predominant carbonate minerals crystallizing from brine-melts are dolomite and ankerite, REE mineralization is typically found to be associated with dolomite and ankerite carbonatite rocks. Even after intensive alteration, the former presence of alkali REE carbonates is evident from the occurrence of these and similar minerals in melt inclusions (Chakhmouradian & Dahlgren 2021). Alkali REE carbonates are rarely preserved in nature due to destabilization in alkali-poor paramagmatic and postmagmatic fluids. They are typically altered to an insoluble residue of monazite and REE-fluorcarbonates such as bastnäsite, alongside a gangue assemblage that records the low-temperature hydrothermal activity (Andersen et al. 2017, Kozlov et al. 2020). Although alteration changes the primary alkali REE mineral assemblage to an alkali-free REE mineral assemblage, the mobility of the REE is strongly limited in an environment that is typically rich in fluoride and phosphate minerals, and buffered to nonacidic conditions by the virtue of being a carbonatite. Essentially, hydrothermal activity redistributes the REE in situ, but it does not transport them over longer distances (e.g., Anenburg et al. 2018, Cangelosi et al. 2020). During carbonatite magma ascent, part of the exsolved synmagmatic fluids is admixed with supergene fluids (groundwater or meteoric water) originating from and interacting with the country rocks (e.g., Broom-Fendley et al. 2016a; Decrée et al. 2015, 2016). These shallow paramagmatic fluids significantly influence the chemistry and temperature of the magmatic and metasomatic fluids, which may induce larger-scale element mobilization and fractionation leading to (*a*) mineralization in association with carbonatites and fenites and (*b*) alteration of certain minerals (e.g., Broom-Fendley et al. 2016b; Decrée et al. 2020a,b). The above-described process is further complicated by the fact that in some cases bastnäsite and monazite are primary magmatic phases. For example, bastnäsite can crystallize from Na-poor carbonatite melts, which is possible when contamination by silicates causes sequestration of Na into aegirine, riebeckite, or arfvedsonite (forming an

Na-K-antiskarn assemblage). These mafic silicates will also sequester Mg and Fe, leading to unexpected REE mineralization within calcite carbonatites. Monazite can crystallize in highly potassic carbonatites where the alkalinity suppresses bastnäsite formation, but the Na contents are insufficient to stabilize burbankite or carbotsernaite (Anenburg et al. 2020b).

A remarkable characteristic of carbonatites is the extreme LREE/HREE fractionation. The four lightest elements (La, Ce, Pr, and Nd) often constitute 99% of the entire REE budget in a carbonatite-hosted LREE deposit, with enrichment factors on the order of 10,000 to 100,000 relative to their respective mantle values. In contrast, the HREE concentrations are typically within the range of average values for the continental crust, with Yb and Lu accounting for only a few parts per million. Various processes contribute to LREE enrichment in carbonatites: (a) preferential partitioning into carbonatite melts within the mantle sources (Foley et al. 2009), (b) preferential partitioning into carbonatite liquids during immiscibility (Martin et al. 2012, 2013; Nabyt et al. 2020), and (c) preferential removal of the HREE during late brine-melt formation with HREE redistribution into fenite aureoles (Andersen et al. 2016, Anenburg et al. 2020b, Broom-Fendley et al. 2017). None of these processes alone can reach the measured enrichment factors for the LREE over the HREE, but it is likely that combinations of known and as-yet-unidentified processes are at play.

10.2. Niobium

Almost all global Nb production comes from pyrochlore, the majority of which is hosted in carbonatite rocks and their weathering products. Pyrochlore is a complex Nb oxide, which shows evidence for magmatic crystallization in carbonatite systems.

Pyrochlore is a liquidus mineral in some experimental carbonatite melts (Kjarsgaard & Mitchell 2008, Mitchell & Kjarsgaard 2002). Experimental work on pyrochlore crystallization in simple carbonatite analog systems [$\text{CaCO}_3\text{-Ca(OH)}_2\text{-NaNbO}_3 \pm \text{NaTaO}_3 \pm \text{TiO}_2 \pm \text{CaF}_2$] at very low pressures (1 atm or 0.1 GPa) has shown that (a) the maximum solubility of Nb in hydrated, fluorinated carbonate liquids is high at ~ 13.8 wt% Nb_2O_5 (equivalent to 17 wt% NaNbO_3) and (b) the crystallization sequence is pyrochlore, fluorite, and calcite in carbonate systems with 20–50 wt% NaNbO_3 . Up to 60 mol% NaNbO_3 was included in these experimental studies because the aim was to saturate the system in this phase in order to determine the solubility of pyrochlore. However, natural carbonatites generally contain only a few thousand parts per million Nb. Nephelinites and melilitites, conjugate immiscible partners to carbonatites in many alkaline complexes, typically contain up to 400 ppm Nb. Therefore, in order to saturate a carbonatite liquid in pyrochlore, Nb must be strongly enriched, and this may occur through (a) relative partitioning of Nb between conjugate silicate and carbonatite magmas or (b) fractional crystallization of carbonate and phosphate minerals until the evolving carbonatite magma reaches pyrochlore saturation. Highly differentiated carbonatites that evolved by fractional crystallization of calcite and probably apatite, and other phases, to alkali- and Fe-carbonate-rich, hydrous- or fluoride-rich compositions are expected to have quite different pyrochlore solubilities and crystallization sequences compared to the experimental analogs.

11. OUTLOOK

Considerable progress has been made over many decades of research involving geology, geochemistry, and experimental petrology in understanding the complexities of carbonatite systems. In this review, we have attempted to present a summary of the current state of understanding of the magma genesis, evolution, and emplacement of carbonatites and associated rocks and fluids.

However, there remain many important questions, resolution of which will require ongoing research into the future.

- How can we unequivocally recognize carbonatite rocks derived directly from partial melting of the upper mantle, as opposed to those that evolved from a parental melt that formed by unmixing from mantle-derived carbonated silicate magmas?
- How much of the carbon in mantle-sourced carbonatite systems was derived by the recycling of crustal carbon via subduction, and how do we recognize this input? Whereas the stable isotopes of C and Ca currently provide no firm answer to this issue, it appears that the B and S isotopic compositions of carbonatites hint at significant contributions of recycled crustal components in the mantle sources of many Phanerozoic carbonatites. Which other isotope systems might prove useful for constraining the amount of crust in the deep sources of carbonated mantle melts?
- How can we resolve the nature and location of the mantle sources of the magmas parental to carbonatites? Isotope geochemistry indicates the involvement of enriched mantle components, but do these reside within the lithospheric mantle or as recycled crustal components within the convecting mantle? How strong is the influence of the tectonic setting on whether a carbonatite system is sourced from the lithosphere or asthenosphere?
- We defined several melt and fluid types: carbonatite melts, brine-melts, and synmagmatic and paramagmatic fluids. The composition of these fluids is often elusive and is only serendipitously preserved, also undergoing postentrapment modification. The boundaries are only loosely defined: Consider a brine-melt mixed with a paramagmatic fluid, both of which derive from the same parental carbonatite melt. What are the relationships between these melt and fluid types, and what is their petrological significance?
- Most carbonatite rocks do not appear to be representative of the melt from which they formed, further complicated by metasomatic reactions with the country rocks, which led to changes of the original bulk compositions and primary mineral assemblages. Are there any systematic changes that can be observed in natural rocks or reproduced in experimental and thermodynamic studies?
- Carbonatite rocks are invariably strongly enriched above continental crustal abundances in LREE, while the HREE are present at generally similar abundances to the average continental crust. What causes this enrichment and the strong LREE/HREE fractionation?
- Experimental studies indicate that key ore minerals of the REE (e.g., apatite and monazite) and Nb (pyrochlore) are highly soluble in carbonatite melts. Despite this, they are usually interpreted as products of crystallization from carbonatite magmas and are often concentrated to economic levels in carbonatite systems. What are the key processes that lead to this natural enrichment of these critical metals in carbonatite systems?

DISCLOSURE STATEMENT

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LITERATURE CITED

- Alt JC, Honnorez J, Laverne C, Emmermann R. 1986. Hydrothermal alteration of a 1 km section through the upper oceanic crust, Deep Sea Drilling Project Hole 504B: mineralogy, chemistry and evolution of seawater-basalt interactions. *J. Geophys. Res.* 91(B10):10309–35
- Amsellem E, Moynier F, Bertrand H, Bouyon A, Mata J, et al. 2020. Calcium isotopic evidence for the mantle sources of carbonatites. *Sci. Adv.* 6:eaba3269
- Andersen AK, Clark JG, Larson PB, Donovan JJ. 2017. REE fractionation, mineral speciation, and supergene enrichment of the Bear Lodge carbonatites, Wyoming, USA. *Ore Geol. Rev.* 89:780–807
- Andersen AK, Clark JG, Larson PB, Neill OK. 2016. Mineral chemistry and petrogenesis of a HFSE(+HREE) occurrence, peripheral to carbonatites of the Bear Lodge alkaline complex, Wyoming. *Am. Mineral.* 101:1604–23
- Andersson M, Malehmir A, Troll VR, Dehghannejad M, Juhlin C, Ask M. 2013. Carbonatite ring-complexes explained by caldera-style volcanism. *Sci. Rep.* 3:1677
- Anenburg M, Burnham AD, Mavrogenes JA. 2018. REE redistribution textures in altered fluorapatite: symplectites, veins, and phosphate-silicate-carbonate assemblages from the Nolans Bore P-REE-Th deposit, Northern Territory, Australia. *Can. Mineral.* 56:331–54
- Anenburg M, Mavrogenes JA. 2018. Carbonatitic versus hydrothermal origin for fluorapatite REE-Th deposits: experimental study of REE transport and crustal “antiskarn” metasomatism. *Am. J. Sci.* 318:335–66
- Anenburg M, Mavrogenes JA, Bennett VC. 2020a. The fluorapatite P-REE-Th vein deposit at Nolans Bore: genesis by carbonatite metasomatism. *J. Petrol.* 61:egaa003
- Anenburg M, Mavrogenes JA, Frigo C, Wall F. 2020b. Rare earth element mobility in and around carbonatites controlled by sodium, potassium, and silica. *Sci. Adv.* 6:eabb6570
- Audétat A, Edmonds M. 2020. Magmatic-hydrothermal fluids. *Elements* 16:401–6
- Ballhaus C. 1995. Is the upper mantle metal-saturated? *Earth Planet. Sci. Lett.* 132:75–86
- Barbosa ESR, Brod JA, Cordeiro PFO, Junqueira-Brod TC, Santos RV, Dantas EL. 2020. Phoscorites of the Salitre I complex: origin and petrogenetic implications. *Chem. Geol.* 535:119463
- Baudouin C, Parat F, Michel T. 2018. CO₂-rich phonolitic melt and carbonatite immiscibility in early stage of rifting: melt inclusions from Hanang volcano (Tanzania). *J. Volcanol. Geotherm. Res.* 358:261–72
- Bell K, Blenkinsop J. 1987. Nd and Sr isotopic compositions of East-African carbonatites: implications for mantle heterogeneity. *Geology* 15:99–102
- Bell K, Simonetti A. 2010. Source of parental melts to carbonatites—critical isotopic constraints. *Mineral. Petrol.* 98:77–89
- Bell K, Tilton GR. 2001. Nd, Pb and Sr isotopic compositions of East African carbonatites: evidence for mantle mixing and plume inhomogeneity. *J. Petrol.* 42:1927–45
- Bell K, Tilton GR. 2002. Probing the mantle: the story from carbonatites. *Eos Trans. AGU* 83:273–77
- Berkési M, Bali E, Bodnar RJ, Szabó Á, Guzmics T. 2020. Carbonatite and highly peralkaline nephelinite melts from Oldoinyo Lengai Volcano, Tanzania: the role of natrite-normative fluid degassing. *Gondwana Res.* 85:76–83
- Bizimis M, Sen G, Salters VJM. 2003. Hf–Nd isotope decoupling in the oceanic lithosphere: constraints from spinel peridotites from Oahu, Hawaii. *Earth Planet. Sci. Lett.* 217:43–58
- Bouvier A, Vervoort JD, Patchett PJ. 2008. The Lu–Hf and Sm–Nd isotopic composition of CHUR: constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. *Earth Planet. Sci. Lett.* 273:48–57
- Brey G. 1978. Origin of olivine melilitites—chemical and experimental constraints. *J. Volcanol. Geotherm. Res.* 3:61–88

- Brooker RA, Kjarsgaard BA. 2011. Silicate–carbonate liquid immiscibility and phase relations in the system $\text{SiO}_2\text{--Na}_2\text{O--Al}_2\text{O}_3\text{--CaO--CO}_2$ at 0.1–2.5 GPa with applications to carbonatite genesis. *J. Petrol.* 52:1281–305
- Broom-Fendley S, Brady AE, Wall F, Gunn G, Dawes W. 2017. REE minerals at the Songwe Hill carbonatite, Malawi: HREE-enrichment in late-stage apatite. *Ore Geol. Rev.* 81:23–41
- Broom-Fendley S, Heaton T, Wall F, Gunn G. 2016a. Tracing the fluid source of heavy REE mineralisation in carbonatites using a novel method of oxygen-isotope analysis in apatite: the example of Songwe Hill, Malawi. *Chem. Geol.* 440:275–87
- Broom-Fendley S, Styles MT, Appleton JD, Gunn G, Wall F. 2016b. Evidence for dissolution-reprecipitation of apatite and preferential LREE mobility in carbonatite-derived late-stage hydrothermal processes. *Am. Mineral.* 101:596–611
- Bühn B, Rankin AH. 1999. Composition of natural, volatile-rich Na–Ca–REE–Sr carbonatitic fluids trapped in fluid inclusions. *Geochim. Cosmochim. Acta* 63:3781–97
- Bühn B, Rankin AH, Schneider J, Dulski P. 2002. The nature of orthomagmatic, carbonatitic fluids precipitating REE,Sr-rich fluorite: fluid-inclusion evidence from the Okorusu fluorite deposit, Namibia. *Chem. Geol.* 186:75–98
- Cangelosi D, Broom-Fendley S, Banks D, Morgan D, Yardley B. 2020. Light rare earth element redistribution during hydrothermal alteration at the Okorusu carbonatite complex, Namibia. *Mineral. Mag.* 84:49–64
- Chakhmouradian AR, Dahlgren S. 2021. Primary inclusions of burbankite in carbonatites from the Fen complex, southern Norway. *Mineral. Petrol.* 115:161–71
- Chakhmouradian AR, Reguir EP, Zaitsev AN. 2016. Calcite and dolomite in intrusive carbonatites. I. Textural variations. *Mineral. Petrol.* 110:333–60
- Chen CF, Liu YS, Foley SF, Ducea MN, He DT, et al. 2016. Paleo-Asian oceanic slab under the North China craton revealed by carbonatites derived from subducted limestones. *Geology* 44:1039–42
- Chen W, Kamenetsky VS, Simonetti A. 2013. Evidence for the alkaline nature of parental carbonatite melts at Oka complex in Canada. *Nat. Commun.* 4:2687
- Church AA, Jones AP. 1995. Silicate–carbonate immiscibility at Oldoinyo Lengai. *J. Petrol.* 36:869–89
- Cooper AF, Palin JM, Collins AK. 2016. Fenitization of metabasic rocks by ferrocarnatites at Haast River, New Zealand. *Lithos* 244:109–21
- Dalton JA, Presnall DC. 1998. The continuum of primary carbonatitic–kimberlitic melt compositions in equilibrium with lherzolite: data from the system $\text{CaO--MgO--Al}_2\text{O}_3\text{--SiO}_2\text{--CO}_2$ at 6 GPa. *J. Petrol.* 39:1953–64
- Dalton JA, Wood BJ. 1993. The compositions of primary carbonate melts and their evolution through wallrock reaction in the mantle. *Earth Planet. Sci. Lett.* 119:511–25
- Dasgupta R, Hirschmann MM. 2006. Melting in the Earth's deep upper mantle caused by carbon dioxide. *Nature* 440:659–62
- Dasgupta R, Hirschmann MM. 2010. The deep carbon cycle and melting in Earth's interior. *Earth Planet. Sci. Lett.* 298:1–13
- Davies DR, Rawlinson N. 2014. On the origin of recent intraplate volcanism in Australia. *Geology* 42:1031–34
- Dawson JB, Pinkerton H, Norton GE, Pyle DM. 1990. Physicochemical properties of alkali carbonatite lavas: data from the 1988 eruption of Oldoinyo Lengai, Tanzania. *Geology* 18:260–63
- de Moor JM, Fischer TP, King PL, Botcharnikov RE, Hervig RL, et al. 2013. Volatile-rich silicate melts from Oldoinyo Lengai volcano (Tanzania): implications for carbonatite genesis and eruptive behavior. *Earth Planet. Sci. Lett.* 361:379–90
- Decrée S, Boulvais P, Cobert C, Baele J-M, Midende G, et al. 2015. Structurally-controlled hydrothermal alteration in the syntectonic Neoproterozoic Upper Ruvubu Alkaline Plutonic Complex (Burundi): implications for REE and HFSE mobilities. *Precambrian Res.* 269:281–95
- Decrée S, Boulvais P, Tack L, André L, Baele J-M. 2016. Fluorapatite in carbonatite-related phosphate deposits: the case of the Matongo carbonatite (Burundi). *Miner. Deposita* 51:453–66
- Decrée S, Cawthorn G, Deloule E, Mercadier J, Frimmel H, Baele J-M. 2020a. Unravelling the processes controlling apatite formation in the Phalaborwa Complex (South Africa) based on combined cathodoluminescence, LA-ICPMS and in-situ O and Sr isotope analyses. *Contrib. Mineral. Petrol.* 175:34

- Decrée S, Savolainen M, Mercadier J, Debaille V, Höhn S, et al. 2020b. Geochemical and spectroscopic investigation of apatite in the Siilinjärvi carbonatite complex: keys to understanding apatite forming processes and assessing potential for rare earth elements. *Appl. Geochem.* 123:104778
- DePaolo DJ, Wasserburg GJ. 1976. Nd isotopic variations and petrogenetic models. *Geophys. Res. Lett.* 3(5):249–52
- Djeddi A, Parat F, Bodinier J-L, Ouzegane K, Dautria J-M. 2021. The syenite–carbonatite complex of Ihouhaouene (Western Hoggar, Algeria): interplay between alkaline magma differentiation and hybridization of cumulus crystal mushes. *Front. Earth Sci.* 8:693
- Doroshkevich AG, Veksler IV, Klemd R, Khromova EA, Izbrodin IA. 2017. Trace-element composition of minerals and rocks in the Belaya Zima carbonatite complex (Russia): implications for the mechanisms of magma evolution and carbonatite formation. *Lithos* 284–285:91–108
- Durand C, Baumgartner LP, Marquer D. 2015. Low melting temperature for calcite at 1000 bars on the join $\text{CaCO}_3\text{-H}_2\text{O}$ —some geological implications. *Terra Nova* 27:364–69
- Eggler DH. 1989. Carbonatites, primary melts, and mantle dynamics. In *Carbonatites: Genesis and Evolution*, ed. K Bell, pp. 561–79. London: Unwin Hyman
- Evans KA, Tomkins AG. 2020. Metamorphic fluids in orogenic settings. *Elements* 16:381–87
- Falloon TJ, Green DH. 1989. The solidus of carbonated, fertile peridotite. *Earth Planet. Sci. Lett.* 94:364–70
- Feng M, Song W, Kynicky J, Smith M, Cox C, et al. 2020. Primary rare earth element enrichment in carbonatites: evidence from melt inclusions in Ulgiu Khiid carbonatite, Mongolia. *Ore Geol. Rev.* 117:103294
- Fischer T, Burnard P, Marty B, Palhol F, Mangasini F, Shaw AM. 2006. *The 2005 and 2006 eruptions of Ol Doinyo Lengai: assessing deep and shallow processes at an active carbonatite volcano using volatile chemistry and fluxes*. Paper presented at AGU Fall Meet., Dec. 11–15, San Francisco, Abstr. V14B-04
- Foley SF. 2011. A reappraisal of redox melting in the Earth's mantle as a function of tectonic setting and time. *J. Petrol.* 52:1363–91
- Foley SF, Yaxley GM, Rosenthal A, Buhre S, Kiseeva ES, et al. 2009. The composition of near-solidus melts of peridotite in the presence of CO_2 and H_2O between 40 and 60 kbar. *Lithos* 112:274–83
- Fortier SM, Hammarstrom JH, Ryker SJ, Day WC, Seal RR. 2019. USGS critical metals review. *Min. Eng.* 71:35–49
- Fosu BR, Ghosh P, Weisenberger TB, Spürigin S, Viladkar SG. 2021. A triple oxygen isotope perspective on the origin, evolution, and diagenetic alteration of carbonatites. *Geochim. Cosmochim. Acta* 299:52–68
- Frisch W, Keusen H-U. 1977. Gardiner intrusion, an ultramafic alkaline complex at Kangerdlugssuaq, East Greenland. *Bull. Geol. Surv. Greenl.* 122:1–62
- Frost DJ, McCammon CA. 2008. The redox state of Earth's mantle. *Annu. Rev. Earth Planet. Sci.* 36:389–420
- Giebel RJ, Marks MAW, Gauert CDK, Markl G. 2019. A model for the formation of carbonatite–phoscorite assemblages based on the compositional variations of mica and apatite from the Palabora Carbonatite Complex, South Africa. *Lithos* 324–325:89–104
- Gittins J, Harmer RE. 1997. What is ferrocarbonatite? A revised classification. *J. Afr. Earth Sci.* 25:159–68
- Grassi D, Schmidt MW. 2011a. Melting of carbonated pelites at 8–13 GPa: generating K-rich carbonatites for mantle metasomatism. *Contrib. Mineral. Petrol.* 162:169–91
- Grassi D, Schmidt MW. 2011b. The melting of carbonated pelites from 70 to 700 km depth. *J. Petrol.* 52:765–89
- Green DH. 2015. Experimental petrology of peridotites, including effects of water and carbon on melting in the Earth's upper mantle. *Phys. Chem. Miner.* 42:95–122
- Green DH, Falloon TJ, Taylor WR. 1987. Mantle-derived magmas—roles of variable source peridotite and variable C–H–O fluid compositions. In *Magmatic Process and Physicochemical Principles*, ed. HS Yoder, BU Mysen, pp. 139–54. University Park, PA: Geochem. Soc.
- Green DH, Wallace ME. 1988. Mantle metasomatism by ephemeral carbonatite melts. *Nature* 336:459–62
- Guzmics T, Berkesi M, Bodnar RJ, Fall A, Bali E, et al. 2019. Natrocarbonatites: a hidden product of three-phase immiscibility. *Geology* 47:527–30
- Guzmics T, Mitchell RH, Szabó C, Berkesi M, Milke R, Abart R. 2011. Carbonatite melt inclusions in co-existing magnetite, apatite and monticellite in Kerimasi calciocarbonatite, Tanzania: melt evolution and petrogenesis. *Contrib. Mineral. Petrol.* 161:177–96

- Guzmics T, Mitchell RH, Szabó C, Berkesi M, Milke R, Ratter K. 2012. Liquid immiscibility between silicate, carbonate and sulfide melts in melt inclusions hosted in co-precipitated minerals from Kerimasi volcano (Tanzania): evolution of carbonated nephelinitic magma. *Contrib. Mineral. Petrol.* 164:101–22
- Guzmics T, Zajacz Z, Mitchell RH, Szabó C, Wälle M. 2015. The role of liquid–liquid immiscibility and crystal fractionation in the genesis of carbonatite magmas: insights from Kerimasi melt inclusions. *Contrib. Mineral. Petrol.* 169:17
- Halama R, McDonough WF, Rudnick RL, Bell K. 2008. Tracking the lithium isotopic evolution of the mantle using carbonatites. *Earth Planet. Sci. Lett.* 265:726–42
- Hamilton DL, Freestone IC, Dawson JB, Donaldson CH. 1979. Origin of carbonatites by liquid immiscibility. *Nature* 279:52–54
- Hammouda T, Chantel J, Manthilake G, Guignard J, Crichton W. 2014. Hot mantle geotherms stabilize calcic carbonatite magmas up to the surface. *Geology* 42:911–14
- Hammouda T, Keshav S. 2015. Melting in the mantle in the presence of carbon: review of experiments and discussion on the origin of carbonatites. *Chem. Geol.* 418:171–88
- Hammouda T, Laporte D. 2000. Ultrafast mantle impregnation by carbonatite melts. *Geology* 28:283–85
- Harmer RE. 1999. The petrogenetic association of carbonatite and alkaline magmatism. Constraints from the Spitskop Complex, South Africa. *J. Petrol.* 40:525–48
- Harmer RE, Gittins J. 1997. The origin of dolomitic carbonatites: field and experimental constraints. *J. Afr. Earth Sci.* 25:5–28
- Hart SR, Staudigel H. 1978. Oceanic crust: age of hydrothermal alteration. *Geophys. Res. Lett.* 5:1009–12
- Hawkesworth CJ, Cawood PA, Dhuime B, Kemp AIS. 2017. Earth's continental lithosphere through time. *Annu. Rev. Earth Planet. Sci.* 45:169–98
- Hegner E, Rajesh S, Willbold M, Müller D, Joachimski M, et al. 2020. Sediment-derived origin of the putative Munnar carbonatite, South India. *J. Asian Earth Sci.* 200:104432
- Hoernle K, Tilton GR, Le Bas MJ, Garbe-Schönberg D. 2002. Geochemistry of oceanic carbonatites compared with continental carbonatites: mantle recycling of oceanic crustal carbonate. *Contrib. Mineral. Petrol.* 142:520–42
- Horton F. 2021. Rapid recycling of subducted sedimentary carbon revealed by Afghanistan carbonatite volcano. *Nat. Geosci.* 14:508–12
- Horton F, Nielsen S, Shu Y, Gagnon A, Blusztajn J. 2021. Thallium isotopes reveal brine activity during carbonatite magmatism. *Geochim. Geophys. Geosyst.* 22:e2020GC009472
- Hou ZQ, Tian SH, Yuan ZX, Xie YL, Yin SP, et al. 2006. The Himalayan collision zone carbonatites in western Sichuan, SW China: petrogenesis, mantle source and tectonic implication. *Earth Planet. Sci. Lett.* 244:234–50
- Hulett SRW, Simonetti A, Rasbury ET, Hemming NG. 2016. Recycling of subducted crustal components into carbonatite melts revealed by boron isotopes. *Nat. Geosci.* 9:904–8
- Humphreys-Williams ER, Zahirovic S. 2021. Carbonatites and global tectonics. *Elements* 17:339–44
- Hutchison W, Babel RJ, Finch AA, Marks MAW, Markl G, et al. 2019. Sulphur isotopes of alkaline magmas unlock long-term records of crustal recycling on Earth. *Nat. Commun.* 10:4208
- Ita J, Stixrude L. 1992. Petrology, elasticity, and composition of the mantle transition zone. *J. Geophys. Res.* 97(B5):6849–66
- Jago BC, Gittins J. 1991. The role of fluorine in carbonatite magma evolution. *Nature* 349:56–58
- Kelemen PB, Manning CE. 2015. Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. *PNAS* 112:E3997–4006
- Keller J, Krafft M. 1990. Effusive natrocarbonatite activity of Oldoinyo Lengai, June 1988. *Bull. Volcanol.* 52:629–45
- Kiseeva ES, Litasov KD, Yaxley GM, Ohtani E, Kamenetsky VS. 2013a. Melting and phase relations of carbonated eclogite at 9–21 GPa and the petrogenesis of alkali-rich melts in the deep mantle. *J. Petrol.* 54:1555–83
- Kiseeva ES, Yaxley GM, Stepanov AS, Tkalčić H, Litasov KD, Kamenetsky VS. 2013b. Metapyroxenite in the mantle transition zone revealed from majorite inclusions in diamonds. *Geology* 41:883–86
- Kjarsgaard BA. 1998. Phase relations of a carbonated high-CaO nephelinite at 0.2 and 0.5 GPa. *J. Petrol.* 39:2061–75

- Kjarsgaard BA, Hamilton DL, Peterson TD. 1995. Peralkaline nephelinite/carbonatite liquid immiscibility: comparison of phase compositions in experiments and natural lavas from Oldoinyo Lengai. In *Carbonatite Volcanism: Oldoinyo Lengai and the Petrogenesis of Natrocarbonatites*, ed. K Bell, J Keller, pp. 163–90. Berlin: Springer-Verlag
- Kjarsgaard BA, Mitchell RH. 2008. Solubility of Ta in the system $\text{CaCO}_3 - \text{Ca}(\text{OH})_2 - \text{NaTaO}_3 - \text{NaNbO}_3 \pm \text{F}$ at 0.1 GPa: implications for the crystallisation of pyrochlore-group minerals in carbonatites. *Can. Mineral.* 46:981–90
- Klemme S. 2010. Experimental constraints on the evolution of iron and phosphorus-rich melts: experiments in the system $\text{CaO-MgO-Fe}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2\text{-H}_2\text{O-CO}_2$. *J. Mineral. Petrol. Sci.* 105:1–8
- Kogarko LN, Plant DA, Henderson CMB, Kjarsgaard BA. 1991. Na-rich carbonate inclusions in perovskite and calzirtite from the Guli intrusive Ca-carbonatite, polar Siberia. *Contrib. Mineral. Petrol.* 109:124–29
- Kono Y, Kenney-Benson C, Hummer D, Ohfuji H, Park C, et al. 2014. Ultralow viscosity of carbonate melts at high pressures. *Nat. Commun.* 5:5091
- Kozlov E, Fomina E, Sidorov M, Shilovskikh V, Bocharov V, et al. 2020. The Petyayan-Vara carbonatite-hosted rare earth deposit (Vuoriyarvi, NW Russia): mineralogy and geochemistry. *Minerals* 10:73
- Kresten P. 1983. Carbonatite nomenclature. *Geol. Rundsch.* 72:389–95
- Kuebler C, Simonetti A, Chen W, Simonetti SS. 2020. Boron isotopic investigation of the Bayan Obo carbonatite complex: insights into the source of mantle carbon and hydrothermal alteration. *Chem. Geol.* 557:119859
- Labidi J, Cartigny P, Moreira M. 2013. Non-chondritic sulphur isotope composition of the terrestrial mantle. *Nature* 501:208–11
- Le Bas MJ. 2008. Fenites associated with carbonatites. *Can. Mineral.* 46:915–32
- Le Maitre RW. 2002. *Igneous Rocks: A Classification and Glossary of Terms*. Cambridge, UK: Cambridge Univ. Press
- Lee W-J, Fanelli MF, Cava N, Wyllie PJ. 2000. Calcicocarbonatite and magnesiocarbonatite rocks and magmas represented in the system $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$ at 0.2 GPa. *Mineral. Petrol.* 68:225–56
- Lee W-J, Wyllie PJ. 1997. Liquid immiscibility between nephelinite and carbonatite from 1.0 to 2.5 GPa compared with mantle melt compositions. *Contrib. Mineral. Petrol.* 127:1–16
- Lee W-J, Wyllie PJ. 1998. Petrogenesis of carbonatite magmas from mantle to crust, constrained by the system $\text{CaO-(MgO + FeO}^*)\text{-(Na}_2\text{O + K}_2\text{O)-(SiO}_2\text{ + Al}_2\text{O}_3\text{ + TiO}_2\text{)-CO}_2$. *J. Petrol.* 39:495–517
- Li WY, Teng FZ, Halama R, Keller J, Klaudius J. 2016. Magnesium isotope fractionation during carbonatite magmatism at Oldoinyo Lengai, Tanzania. *Earth Planet. Sci. Lett.* 444:26–33
- Løvik AN, Hagelūken C, Wäger P. 2018. Improving supply security of critical metals: current developments and research in the EU. *Sustain. Mater. Technol.* 15:9–18
- Lustrino M, Ronca S, Caracausi A, Bordenca CV, Agostini S, Faraone DB. 2020. Strongly SiO_2 -undersaturated, CaO-rich kamafugitic Pleistocene magmatism in Central Italy (San Venanzo volcanic complex) and the role of shallow depth limestone assimilation. *Earth-Sci. Rev.* 208:103256
- Marschall HR, Wanless VD, Shimizu N, Pogge von Strandmann PAE, Elliott T, Monteleone BD. 2017. The boron and lithium isotopic composition of mid-ocean ridge basalts and the mantle. *Geochim. Cosmochim. Acta* 207:102–38
- Martin LHJ, Schmidt MW, Mattsson HB, Guenther D. 2013. Element partitioning between immiscible carbonatite and silicate melts for dry and H_2O -bearing systems at 1–3 GPa. *J. Petrol.* 54:2301–38
- Martin LHJ, Schmidt MW, Mattsson HB, Ulmer P, Hametner K, Günther D. 2012. Element partitioning between immiscible carbonatite–kamafugite melts with application to the Italian ultrapotassic suite. *Chem. Geol.* 320–321:96–112
- Massuyeau M, Gardés E, Rogerie G, Aulbach S, Tappe S, et al. 2021. MAGLAB: a computing platform connecting geophysical signatures to melting processes in Earth's mantle. *Phys. Earth Planet. Inter.* 314:106638
- Matjuschkin V, Woodland AB, Yaxley GM. 2018. Methane-bearing fluids in the upper mantle: an experimental approach. *Contrib. Mineral. Petrol.* 174:1
- McKenzie D, Jackson J, Priestley K. 2005. Thermal structure of oceanic and continental lithosphere. *Earth Planet. Sci. Lett.* 233:337–49

- Milani L, Bolhar R, Frei D, Harlov DE, Samuel VO. 2017. Light rare earth element systematics as a tool for investigating the petrogenesis of phoscorite-carbonatite associations, as exemplified by the Phalaborwa Complex, South Africa. *Miner. Deposita* 52:1105–25
- Mitchell RH. 2005. Carbonatites and carbonatites and carbonatites. *Can. Mineral.* 43:2049–68
- Mitchell RH. 2009. Peralkaline nephelinite–natrocarbonatite immiscibility and carbonatite assimilation at Oldoinyo Lengai, Tanzania. *Contrib. Mineral. Petrol.* 158:589–98
- Mitchell RH, Dawson JB. 2012. Carbonate–silicate immiscibility and extremely peralkaline silicate glasses from Nasira cone and recent eruptions at Oldoinyo Lengai Volcano, Tanzania. *Lithos* 152:40–46
- Mitchell RH, Kjarsgaard BA. 2002. Solubility of niobium in the system $\text{CaCO}_3\text{--Ca(OH)}_2\text{--NaNbO}_3$ at 0.1 GPa pressure. *Contrib. Mineral. Petrol.* 144:93–97
- Mitchell RH, Kjarsgaard BA. 2011. Experimental studies of the system $\text{Na}_2\text{CO}_3\text{--CaCO}_3\text{--MgF}_2$ at 0.1 GPa: implications for the differentiation and low-temperature crystallization of natrocarbonatite. *J. Petrol.* 52:1265–80
- Nabyl Z, Massuyeau M, Gaillard F, Tuduri J, Iacono-Marziano G, et al. 2020. A window in the course of alkaline magma differentiation conducive to immiscible REE-rich carbonatites. *Geochim. Cosmochim. Acta* 282:297–323
- Nelson DR, Chivas AR, Chappell BW, McCulloch MT. 1988. Geochemical and isotopic systematics in carbonatites and implications for the evolution of ocean-island sources. *Geochim. Cosmochim. Acta* 52:1–17
- Nielsen TFD. 1981. The ultramafic cumulate series, Gardiner complex, East Greenland. *Contrib. Mineral. Petrol.* 76:60–72
- Nielsen TFD, Solovova IP, Veksler IV. 1997. Parental melts of melilitolite and origin of alkaline carbonatite: evidence from crystallised melt inclusions, Gardiner complex. *Contrib. Mineral. Petrol.* 126:331–44
- Nielsen TFD, Veksler IV. 2002. Is natrocarbonatite a cognate fluid condensate? *Contrib. Mineral. Petrol.* 142:425–35
- Özkan M, Çelik ÖF, Marzoli A, Çörtük RM, Billor MZ. 2021. The origin of carbonatites from the eastern Armutlu Peninsula (NW Turkey). *J. Geol. Soc.* 178(6):jgs2020-171
- Panina LI, Motorina IV. 2008. Liquid immiscibility in deep-seated magmas and the generation of carbonatite melts. *Geochem. Int.* 46:448–64
- Peterson TD. 1989. Peralkaline nephelinites. I. Comparative petrology of Shombole and Oldoinyo L'engai, East Africa. *Contrib. Mineral. Petrol.* 101:458–78
- Pilet S, Baker MB, Stolper EM. 2008. Metasomatized lithosphere and the origin of alkaline lavas. *Science* 320:916–19
- Pintér Z, Foley SF, Yaxley GM, Rosenthal A, Rapp RP, et al. 2021. Experimental investigation of the composition of incipient melts in upper mantle peridotites in the presence of CO_2 and H_2O . *Lithos* 396–397:106224
- Pirajno F. 1994. Mineral resources of anorogenic alkaline complexes in Namibia: a review. *Aust. J. Earth Sci.* 41:157–68
- Plank T, Langmuir CH. 1998. The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chem. Geol.* 145:325–94
- Poli S, Franzolin E, Fumagalli P, Crottini A. 2009. The transport of carbon and hydrogen in subducted oceanic crust: an experimental study to 5 GPa. *Earth Planet. Sci. Lett.* 278:350–60
- Prokopyev IR, Doroshkevich AG, Zhumadilova DV, Starikova AE, Nugumanova YN, Vladyskin NV. 2021. Petrogenesis of Zr–Nb (REE) carbonatites from the Arbarastakh complex (Aldan Shield, Russia): mineralogy and inclusion data. *Ore Geol. Rev.* 131:104042
- Rankin AH. 1975. Fluid inclusion studies in apatite from carbonatites of the Wasaki area of western Kenya. *Lithos* 8:123–36
- Rass IT, Petrenko DB, Koval'chuk EV, Yakushev AI. 2020. Phoscorites and carbonatites: relations, possible petrogenetic processes, and parental magma, with reference to the Kovdor Massif, Kola Peninsula. *Geochem. Int.* 58:753–78
- Rass IT, Plechov PY. 2000. Melt inclusions in olivines from the olivine-melilitite rock of the Guli massif, northwestern Siberian platform. *Dokl. Earth Sci.* 375:389–92

- Rohrbach A, Ghosh S, Schmidt MW, Wijbrans CH, Klemme S. 2014. The stability of Fe–Ni carbides in the Earth's mantle: evidence for a low Fe–Ni–C melt fraction in the deep mantle. *Earth Planet. Sci. Lett.* 388:211–21
- Rohrbach A, Schmidt MW. 2011. Redox freezing and melting in the Earth's deep mantle resulting from carbon–iron redox coupling. *Nature* 472:209–12
- Rooney TO, Nelson WR, Ayalew D, Hanan B, Yirgu G, Kappelman J. 2017. Melting the lithosphere: metasomes as a source for mantle-derived magmas. *Earth Planet. Sci. Lett.* 461:105–18
- Rudnick RL, McDonough WF, Chappell BW. 1993. Carbonatite metasomatism in the northern Tanzanian mantle: petrographic and geochemical characteristics. *Earth Planet. Sci. Lett.* 114:463–75
- Ryabchikov ID, Kogarko LN. 2016. Deep differentiation of alkali ultramafic magmas: formation of carbonatite melts. *Geochem. Int.* 54:739–47
- Salters VJM, Stracke A. 2004. Composition of the depleted mantle. *Geochem. Geophys. Geosyst.* 5:Q05B07
- Savard JJ, Mitchell RH. 2021. Petrology of ijolite series rocks from the Prairie Lake (Canada) and Fen (Norway) alkaline rock-carbonatite complexes. *Lithos* 396–397:106188
- Schmidt MW, Wiedendorfer D. 2018. Carbonatites in oceanic hotspots. *Geology* 46:435–38
- Schumann D, Martin RF, Fuchs S, de Fourestier J. 2019. Silicocarbonatitic melt inclusions in fluorapatite from the Yates prospect, Otter Lake, Québec: evidence of marble anatexis in the central metasedimentary belt of the Grenville Province. *Can. Mineral.* 57:583–604
- Sharygin VV, Kamenetsky VS, Zaitsev AN, Kamenetsky MB. 2012. Silicate–natrocarbonatite liquid immiscibility in 1917 eruption combeite–wollastonite nephelinite, Oldoinyo Lengai Volcano, Tanzania: melt inclusion study. *Lithos* 152:23–39
- Shaw CSJ. 2018. Evidence for the presence of carbonate melt during the formation of cumulates in the Colli Albani Volcanic District, Italy. *Lithos* 310–311:105–19
- Sieber MJ, Hermann J, Yaxley GM. 2018. An experimental investigation of C–O–H fluid-driven carbonation of serpentinites under forearc conditions. *Earth Planet. Sci. Lett.* 496:178–88
- Sieber MJ, Yaxley GM, Hermann J. 2020. Investigation of fluid-driven carbonation of a hydrated, forearc mantle wedge using serpentinite cores in high-pressure experiments. *J. Petrol.* 61:egaa035
- Slezak P, Spandler C. 2020. Petrogenesis of the Gifford Creek Carbonatite Complex, Western Australia. *Contrib. Mineral. Petrol.* 175:28
- Song W, Xu C, Veksler IV, Kynicky J. 2016. Experimental study of REE, Ba, Sr, Mo and W partitioning between carbonatitic melt and aqueous fluid with implications for rare metal mineralization. *Contrib. Mineral. Petrol.* 171:1
- Stagno V, Ojwang DO, McCammon CA, Frost DJ. 2013. The oxidation state of the mantle and the extraction of carbon from Earth's interior. *Nature* 493:84–88
- Stracke A. 2012. Earth's heterogeneous mantle: a product of convection-driven interaction between crust and mantle. *Chem. Geol.* 330–331:274–99
- Streckeisen A. 1980. Classification and nomenclature of volcanic rocks, lamprophyres, carbonatites and melilitic rocks IUGS Subcommittee on the Systematics of Igneous Rocks. *Geol. Rundsch.* 69:194–207
- Sun J, Zhu XK, Belshaw NS, Chen W, Doroshkevich AG, et al. 2021. Ca isotope systematics of carbonatites: insights into carbonatite source and evolution. *Geochem. Perspect. Lett.* 17:11–15
- Sweeney RJ. 1994. Carbonatite melt compositions in the Earth's mantle. *Earth Planet. Sci. Lett.* 128:259–70
- Tappe S, Massuyeau M, Smart KA, Woodland AB, Gussone N, et al. 2021. Sheared peridotite and megacryst formation beneath the Kaapvaal craton: a snapshot of tectonomagmatic processes across the lithosphere–asthenosphere transition. *J. Petrol.* 62(8):egab046
- Tappe S, Romer RL, Stracke A, Steinfeldt A, Smart KA, et al. 2017. Sources and mobility of carbonate melts beneath cratons, with implications for deep carbon cycling, metasomatism and rift initiation. *Earth Planet. Sci. Lett.* 466:152–67
- Tappe S, Stracke A, van Acken D, Strauss H, Luguet A. 2020. Origins of kimberlites and carbonatites during continental collision—insights beyond decoupled Nd–Hf isotopes. *Earth-Sci. Rev.* 208:103287
- Teague AJ, Seward TM, Harrison D. 2008. Mantle source for Oldoinyo Lengai carbonatites: evidence from helium isotopes in fumarole gases. *J. Volcanol. Geotherm. Res.* 175:386–90
- Thomsen TB, Schmidt MW. 2008. Melting of carbonated pelites at 2.5–5.0 GPa, silicate–carbonatite liquid immiscibility, and potassium–carbon metasomatism of the mantle. *Earth Planet. Sci. Lett.* 267:17–31

- Thomson AR, Walter MJ, Kohn SC, Brooker RA. 2016. Slab melting as a barrier to deep carbon subduction. *Nature* 529:76–79
- Tilton GR, Bell K. 1994. Sr–Nd–Pb isotope relationships in Late Archean carbonatites and alkaline complexes: applications to the geochemical evolution of Archean mantle. *Geochim. Cosmochim. Acta* 58:3145–54
- Treiman AH, Essene EJ. 1985. The Oka carbonatite complex, Quebec: geology and evidence for silicate–carbonate liquid immiscibility. *Am. Mineral.* 70:1101–13
- Tsuno K, Dasgupta R. 2015. Fe–Ni–Cu–C–S phase relations at high pressures and temperatures—the role of sulfur in carbon storage and diamond stability at mid- to deep-upper mantle. *Earth Planet. Sci. Lett.* 412:132–42
- Tucker RD, Belkin HE, Schulz KJ, Peters SG, Horton F, et al. 2012. A major light rare-earth element (LREE) resource in the Khanneshin Carbonatite Complex, Southern Afghanistan. *Econ. Geol.* 107:197–208
- Veksler IV, Dorfman AM, Dulski P, Kamenetsky VS, Danyushevsky LV, et al. 2012. Partitioning of elements between silicate melt and immiscible fluoride, chloride, carbonate, phosphate and sulfate melts, with implications to the origin of natrocarbonatite. *Geochim. Cosmochim. Acta* 79:20–40
- Veksler IV, Keppler H. 2000. Partitioning of Mg, Ca, and Na between carbonatite melt and hydrous fluid at 0.1–0.2 GPa. *Contrib. Mineral. Petrol.* 138:27–34
- Veksler IV, Nielsen TFD, Sokolov SV. 1998. Mineralogy of crystallized melt inclusions from Gardiner and Kovdor ultramafic alkaline complexes: implications for carbonatite genesis. *J. Petrol.* 39:2015–31
- Wallace ME, Green DH. 1988. An experimental determination of primary carbonatite magma composition. *Nature* 335:343–46
- Walter BF, Giebel RJ, Steele-MacInnis M, Marks MAW, Kolb J, Markl G. 2021. Fluids associated with carbonatitic magmatism: a critical review and implications for carbonatite magma ascent. *Earth-Sci. Rev.* 215:103509
- Walter BF, Steele-MacInnis M, Giebel RJ, Marks MAW, Markl G. 2020. Complex carbonate–sulfate brines in fluid inclusions from carbonatites: estimating compositions in the system H_2O – Na – K – CO_3 – SO_4 – Cl . *Geochim. Cosmochim. Acta* 277:224–42
- Wei C-W, Xu C, Chakhmouradian AR, Brenna M, Kynicky J, Song W-L. 2020. Carbon–strontium isotope decoupling in carbonatites from Caotan (Qinling, China): implications for the origin of calcite carbonatite in orogenic settings. *J. Petrol.* 61:egaa024
- Weidendorfer D, Schmidt MW, Mattsson HB. 2017. A common origin of carbonatite magmas. *Geology* 45:507–10
- Weidendorfer D, Schmidt MW, Mattsson HB. 2019. Mineral resorption triggers explosive mixed silicate–carbonatite eruptions. *Earth Planet. Sci. Lett.* 510:219–30
- Woolley AR. 1982. A discussion of carbonatite evolution and nomenclature, and the generation of sodic and potassic fenites. *Mineralog. Mag.* 46:13–17
- Woolley AR, Church AA. 2005. Extrusive carbonatites: a brief review. *Lithos* 85:1–14
- Woolley AR, Kempe DRC. 1989. Carbonatites: nomenclature, average chemical compositions, and element distribution. In *Carbonatites: Genesis and Evolution*, ed. K Bell, pp. 1–14. London: Unwin Hyman
- 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. *Can. Mineral.* 46:741–52
- Xu C, Kynicky J, Chakhmouradian AR, Campbell IH, Allen CM. 2010. Trace-element modeling of the magmatic evolution of rare-earth-rich carbonatite from the Miaoya deposit, Central China. *Lithos* 118:145–55
- Yaxley GM, Crawford A, Green D. 1991. Evidence for carbonatite metasomatism in spinel peridotite xenoliths from Western Victoria, Australia. *Earth Planet. Sci. Lett.* 107:305–17
- Yaxley GM, Ghosh S, Kiseeva ES, Mallik A, Spandler C, et al. 2020. CO_2 -rich melts in Earth. In *Deep Carbon: Past to Present*, ed. BN Orcutt, I Daniel, R Dasgupta, pp. 129–62. Cambridge, UK: Cambridge Univ. Press
- Yaxley GM, Green D. 1994. Experimental demonstration of refractory carbonate-bearing eclogite and siliceous melt in the subduction regime. *Earth Planet. Sci. Lett.* 128:313–25
- Ying Y-C, Chen W, Simonetti A, Jiang S-Y, Zhao K-D. 2020. Significance of hydrothermal reworking for REE mineralization associated with carbonatite: constraints from in situ trace element and C–Sr isotope study

- of calcite and apatite from the Miaoya carbonatite complex (China). *Geochim. Cosmochim. Acta* 280:340–59
- Zaitsev AN, Keller J. 2006. Mineralogical and chemical transformation of Oldoinyo Lengai natrocarbonatites, Tanzania. *Lithos* 91:191–207
- Zeng RS, MacKenzie WS. 1984. Preliminary report on the system $\text{NaAlSiO}_4\text{-KAlSiO}_4\text{-SiO}_2\text{-H}_2\text{O}$ at $\text{PH}_2\text{O} = 5$ kbar. *Bull. Mineralog.* 107:571–755
- Zindler A, Hart SR. 1986. Chemical geodynamics. *Annu. Rev. Earth Planet. Sci.* 14:493–571
-

RELATED RESOURCES

- Yaxley GM, Anenburg M, Timmerman S, eds. 2021. Carbonatites. *Elements* 17(5)