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Global Sr-Nd-Os isotopic and platinum-group element systematic of mantle-derived carbonatites

Globální Sr-Nd-Os izotopická systematika a prvky platinové skupiny v karbonatitech

Doctoral thesis

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To the best of my knowledge, I declare that the Ph.D. thesis titled "*Global Sr-Nd-Os isotopic and platinum-group element systematics of mantle-derived carbonatites*" is original work and has not been handed to another jury in this or a similar form.

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Chapter 1:

A carbonatite saga

1.1. Carbonatites and their isotope systematics: Introduction

Carbonatites are rather rarely occurring igneous rocks formed in the upper mantle or in the lower crust from carbonate-rich parental melts which themselves are mostly derived from the mantle. The currently known occurrences of carbonatites span the emplacement ages from the Archean to present-day (Digis, 2024). Carbonatite melts are formed at very low partial melting degrees and can separate from their residue at a melt fraction as small as 0.02% (Hunter and McKenzie, 1989). In fact, carbonatites may represent the first melt to appear, followed by melilitites and kimberlites (Lee and Wyllie, 1998; Yaxley et al., 2021). The former rock types are almost exclusively emplaced in continental intraplate settings such as cratons or margins, compared to infrequent occurrences at oceanic settings, and are often associated with active extensional environments (Fig. 1.1). However, the exact mode of genesis of carbonatites is still debated (Yaxley et al., 2021 and references therein). As a consequence of their low viscosity and density (e.g., Dobson et al., 1996; Giordano and Dingwell, 2003; Kono et al., 2014; Treiman and Schedl, 1983), carbonatite melts are capable of migrating upwards from their source at low melt fractions, carrying significant amounts of volatiles, and behaving as a remarkable metasomatic agent (e.g., Rudnick et al., 1993; Yaxley et al., 2019). Besides, carbonatites have an impact on the global economy due to their unique capability to concentrate so-called critical elements at substantial levels such as rare earth elements, niobium, gallium, or phosphates (e.g., Berger et al., 2009; Verplanck and Gosen, 2011). These elements are used in a wide range of high-technology applications and electronic devices, defense systems, agriculture, or the aerospace industry, and their economic availability is therefore of key importance for society (Simandl and Paradis, 2018).



Fig. 1.1. Map of worldwide carbonatite occurrences (compiled from Copernicus program). Approximate location of cratonic regions, Precambrian shields, and carbonatite locations redrawn from Liu et al. (2023) and Woolley and Kjarsgaard (2008a).

Once carbonatites reach (near)surface conditions, they are utterly sensitive to meteoritic-water and hydrothermal alteration, notably in the case of natrocarbonatites (e.g., Guzmics et al., 2011), which might be one of the reasons for their rare occurrences in the geological record. The global distribution of carbonatites is spatially and temporally related. First, carbonatites are associated with major crustal events related to the formation and/or breakup of (super)continents. In this respect, about 70% of all currently known carbonatites can be correlated with these events which are tightly linked with the U-Pb zircon ages peaks (Hawkesworth et al., 2020; Fig. 2.6). Second, there is a growing number of carbonatite occurrence from Archean to recent (distribution power-law growth curve $r^2 = 0.94$; Liu et al., 2023). This can be caused by increasing amounts of material required for carbonatite formation due to the dominant role of carbon recycled at the subduction zones since the

primordial mantle (non-modified mantle formed during the early stage of the Earth's history) would not be capable of supplying large amounts of carbonate-rich melts (Dasgupta, 2013). Also, younger carbonatites have a greater likelihood to escape weathering and alteration until they are discovered, compared to the older ones. Due to a distinctively different composition of carbonatitic melts and mantle/crustal lithologies, carbonatitic melts will largely modify their surroundings during their migration at upper mantle conditions or ascent towards the Earth's crust. A relatively smaller portion of carbonatites can also be "consumed" during these events leaving behind locally metasomatized areas. However, a non-negligible proportion of carbonatites formed in the upper mantle may have never left their immediate vicinity and could have vanished near their place of origin (Bell et al., 1998; Woolley, 1989a,b). Such behavior seems to be related to the limited number of carbonatite bodies being present on the Earth's surface. In order for carbonatite magma to reach the surface, it has to be presented in large quantities and/or with sufficient steady supply, or its conduit/chamber has to be protected by lining reaction products (wehrlite; Harmer and Gittins, 1997). These processes are described in detail lower.

The first brief description of carbonatites was presented by Bose (1884) while the first carbonatites described as magmatic rocks were those found at Alnö and Fen carbonatite complexes in Sweden and Norway by Högbom, (1895) and Brøgger, (1920), respectively. The dissenting opinions in the scientific community were dispersed when Wyllie and Tuttle (1960) published an intriguing experimental study showing that calcite can crystalize at magmatic conditions at a temperature around 650 °C and pressure of 0.1 GPa. The interest in the carbonatites was then relented but increased again with the awareness of Oldoinyo Lengai in Tanzania, the sole present-day active (natro)carbonatite volcano.

As carbonatites have only been known for a little over 100 years, their genesis and source of origin have been the subject of a long and vigorous debate for decades. This is especially because vast modifications in chemical and mineralogical compositions during magma ascent and post-emplacement may occur not only in the case of carbonatite melts but also in the ambient environment. These processes are still relatively poorly understood and make the identification of all processes related to the carbonatite magma origin and emplacement more challenging. Nevertheless, there is an overall consensus in the scientific community that one of the most powerful tools for the clarification of these outstanding questions is represented by radiogenic and stable isotope systematics. Since the gradual discoveries of isotopic systems, they have been widely used in geochemistry leading to breakthrough discoveries on the source (e.g., roles of depleted/enriched mantle source and recycled crust) and evolution (e.g., fractional crystallization, assimilation) of magmatic rocks (e.g., DePaolo, 2012; Dickin, 2018; Eiler et al., 2014; Faure, 1987; White and Hofmann, 1982). The first use of the word "isotope" came from Soddy (1913) when he noticed with his colleague and former student Lord Alexander Fleck (Kauffman, 1982) that there was a strong affinity between uranium and thorium salts.

In fact, the similar chemical properties of thorium and ionium (the historical name for ^{230}Th) were noted even earlier by Boltwood in 1908 based on the character of those two substances which resulted in the discovery of the heaviest isotopic decay chains (U-Th-Pb). Subsequently, other isotopic systems joined the zoo of radiogenic isotope systems. The rubidium-strontium isotope dating ($^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$) method in geological material was introduced by Otto Hahn (Hahn et al., 1943; Hahn and Walling, 1938). The significant advances in the Rb–Sr method were delayed by a Second World War, and the same destiny was predestined to Sm–Nd isotope systematics which was not described until 1974 by Lungmair. Based on this paper, the seminal treatise by DePaolo and Wasserburg (1976) that is valid until today was published. At about the same time, Allègre and Luck (1980) described osmium isotope systematics based on the decay of ^{187}Re to ^{187}Os as an important geological tracer. Similarly, much earlier, the stable isotope systematics of oxygen were described by Urey in 1947 which laid the foundation for geochronology and paleoclimatology. Urey with others (e.g., McCrea, 1950) described the basics of the carbon isotope cycle in later years, but the major breakthrough in carbon isotope geochemistry came in 1953 by Craig.

1.2. Nomenclature and petrogenesis of carbonatites

By the generally accepted nomenclature, carbonatites are defined as igneous rocks, intrusive or extrusive, with >50 modal % of magmatic carbonate minerals (Streckeisen, 1974) derived from **mantle** and less than 20 wt.% SiO_2 (Le Maitre, 2002) although competing schemes for nomenclature of carbonatites exist (Mitchell, 2005; Yaxley et al., 2022). Carbonatites are commonly classified into six types defined on the basis of the dominant carbonate phase:

1. **Calciocarbonatite** (also calcite carbonatite) that consists mainly of calcite with two different rock textures: *sövite* – coarse-grained and *alvikite* – fine-grained.
2. **Magnesiocarbonatite** (also dolomite carbonatite) consists mainly of dolomite. Earlier. This rock type was also called *beforsite*. Firstly described by von Eckermann in 1928 as a mica-carbonate-dike discovered during East Coast Railway construction between Bergerforsen and Stavre in Sweden (near Alnö). Streckeisen, (1974) suggested abandoning this term and using dolomite carbonatite instead.
3. **Ferrocronatite** (ankerite carbonatite) that consists mainly of ankerite. The term **ferruginous carbonatite** is usually used for Fe-rich carbonatite where the iron is not solely hosted by ankerite, but rather in Fe-(oxy)hydroxides such as magnetite and hematite. In this respect, *rödberg* (or *rödberg* or *red rock*) is hydrothermally altered hematite-rich carbonatite from the Fen Carbonatite Complex in Norway. Originally the term *rödberg* was used for a local weathered rock from the Telemark area, but nowadays it is used to describe similar types of rocks also from other carbonatite sites (e.g., Lemitar Mountains, USA, McLemore, 1987; Yangibana, Western Australia,

Slezak et al., 2021; Amba Dongar, India, Viladkar, 2018). The former name of ferrocarbonatite and magnesiocarbonatite was *rauhaugite*, which was divided into type I (Fe-rich) and II (Mg-rich) by Sæther (1957) and later renamed on the basis of their dominant carbonate phase.

4. **Natrocronatite** is characterized by the predominance of alkalis over CaO-MgO-FeO_t [(Na₂O + K₂O) > (CaO + MgO + FeO)]. According to the prevailing content of sodium or potassium, these carbonatites are sometimes called with respect to predominant carbonate phases *nyererite* or *fairchildite* (*gregoryite*; Mitchell and Gittins, 2022), respectively. Overall, natrocronatites are extremely rare rocks, because of their well-known instability under atmospheric conditions, forming gray-white powder on a lava surface within a few days after the eruption (Zaitsev and Keller, 2006). Therefore, it is very hard to assess the spatial occurrence of this carbonatite in the Earth's history.
5. **Rare earth element (REE) carbonatites** with various CaO, MgO, and FeO_t contents containing at least 1 wt. % of REE₂O₃ (REE represents sum of all REE oxides; Jones et al., 2013).
6. **Silicocarbonatites** are considered as primary magmatic rocks containing a maximum of 20 wt.% of SiO₂ (Le Maitre, 2002) that consist of both silicate (e.g., olivine, clinopyroxene, feldspar, mica, and amphibole) and carbonate (calcite, dolomite, ankerite) mineral phases which are texturally related suggesting their co-existence. With respect to their silica contents, silicocarbonatites can be divided into *kåsenite*, *hollaite*, and *ringite* (Marien, 2019). On the other hand, the so-called **silicified carbonatites** are rocks with anomalously high SiO₂ contents at given very low Al₂O₃ or MgO representing rock types that have been affected by late-stage hydrothermal alteration by SiO₂-rich fluids. Therefore, silicified carbonatite is considered to be a product of later magmatic/hydrothermal activity, and its stable isotope (e.g., C–O) composition can be largely modified in this respect. On the other hand, silicified carbonatites typically contain secondary fluorite, quartz, baryte, or strontianite (SrCO₃; Viladkar, 2019) and therefore, can represent an important source for many rare elements.

Apart from mantle-derived carbonatites, there is a piece of growing evidence for the presence of crustal-derived carbonatites (Hegner et al., 2020; Wu et al., 2022). This is because, during the partial melting of calcite- and dolomite-rich lithologies (e.g., limestone, marble) at upper crustal pressures at temperatures around 650 °C, the so-called **anatectic carbonatites** can be formed (Durand et al., 2015). Partial melting can be further facilitated by metamorphic or hydrothermal fluids often rich in silica causing notable enrichment in silicate or oxide minerals such as magnetite or garnet (Yaxley et al., 2022 and references therein) in the target lithologies.

Several silicate rock lithologies that are intimately associated with the interaction of carbonatitic melts/fluids are well-known. For example, **fenites** are alkali-rich metasomatized rocks that commonly comprise of K-feldspar, albite, alkali pyroxene, and alkali amphiboles (Hogarth and LaPointe, 1984) and indicate the presence of carbonate-rich melts/fluids in their immediate vicinity

(see Chapter 1.4 for more details on this peculiar type of rock). Another metasomatized rock formed from the interaction of carbonatitic melt/fluid with a silica-rich lithology is the so-called **antiskarn**. These calc-silicate rocks consist mainly of quartz, garnet, diopside, wollastonite, calcite, and dolomite (Anenburg and Mavrogenes, 2018). An antiskarn reaction leads to the REE enrichment across the whole metasomatized rock, typically with large variations over a small area (mm²) sometimes associated with re-mobilization and local enrichment of REE (Voropaeva et al., 2024). Therefore, antiskarns are economically interesting and potentially perspective but, at the same time, they represent a challenging rock type for REE extraction due to their very complex mineralogy.

Another example of silicate rock associated with carbonatites is (ultra)mafic rock rich in phosphates called **phoscorite**, often forming a girdle, ring, or arcuate zones or veins around or within the centers of carbonatite bodies (Krasnova et al., 2004b). The phoscorites consist of magnetite, apatite, diopside, phlogopite, calcite, dolomite, and forsterite (Fontana, 2006). The mineralogical and geochemical similarities with associated carbonatites indicate their close mutual relationship and origin through the differentiation of the same Fe–P–Si-rich carbonated melts separated by either liquid immiscibility or through fractional crystallization and/or crystal accumulation (Krasnova et al., 2004a). However, the occurrence of phoscorites is rather rare as there are only several tens of phoscorite occurrences around the world (Sarbas and Nohl, 2008) with one of the best examples documented from the Phalaborwa Complex, South Africa, also targeted by this Ph.D. thesis.

In addition to dominant carbonate phases, carbonatites are characterized by the common presence of apatite, baryte, magnetite, fluorite, phlogopite, and pyrochlore that is primarily responsible for Nb enrichment, but overall very low contents of sulfides (note however, a unique presence of Cu-rich carbonatite at Phalaborwa). More rarely, carbonatites also contain olivine, clinopyroxene, or mica whereas columbite, monazite, zircon (or baddeleyite), xenotime, thorite, thorianite, and uraninite represent the accessory phases found in some carbonatites (e.g., Christy et al., 2021).

There are several approaches combining chemical composition with mineralogy that are used to define the type of carbonatite: **(1)** different carbonate weight proportions calculated from bulk chemistry and plotted either as a binary representation as suggested from the recognition of calciocarbonatite and magnesiocarbonatite by Streckeisen, (1974; see Fig. 1.2a), **(2)** relative proportions of bulk-rock CaO, MgO, FeO_t and MnO contents plotted in the ternary diagram (Woolley, 1982; Fig. 1.2b), **(3)** defining bulk-rock SiO₂ contents to recognize presence of silicocarbonatites in the ternary diagram (Srivastava, 1993; Fig. 1.2c), **(4)** using bulk-rock molar rather than weight proportion of selected oxides (Fig. 1.2d) as suggested by Gittins and Harmer (1997). Finally, as pointed out by (e.g., Mitchell and Gittins, 2022; Viladkar, 2019), carbonatites should be rather classified using the nomenclature based on detailed mineralogy **(5)** rather than rely on bulk-rock chemistry which might be sometimes misleading due to common late-stage addition and /or

modification of non-carbonate phases. For example, ferrocarbonatite should solely be recognized based on petrography (ankerite and siderite), but in many cases, iron is determined as total Fe and later re-calculated into Fe^{2+} and Fe^{3+} . However, most of the Fe-bearing minerals presented in carbonatites such as magnetite are subjected to hematitization during which the significant proportion of ferrous and ferric iron in the sample was modified and plots utilizing Fe^{2+} may thus be displayed incorrectly. Another example can be demonstrated in the false recognition of magnesiocarbonatite based solely on MgO content from bulk analysis. This is because a significant amount of Mg can be hosted by olivine and/or clinopyroxene which might be presented in some carbonatites. While olivine can be rather accessory in many instances, it has been recognized that even a small amount of forsteritic olivine may largely change the bulk-rock MgO contents.

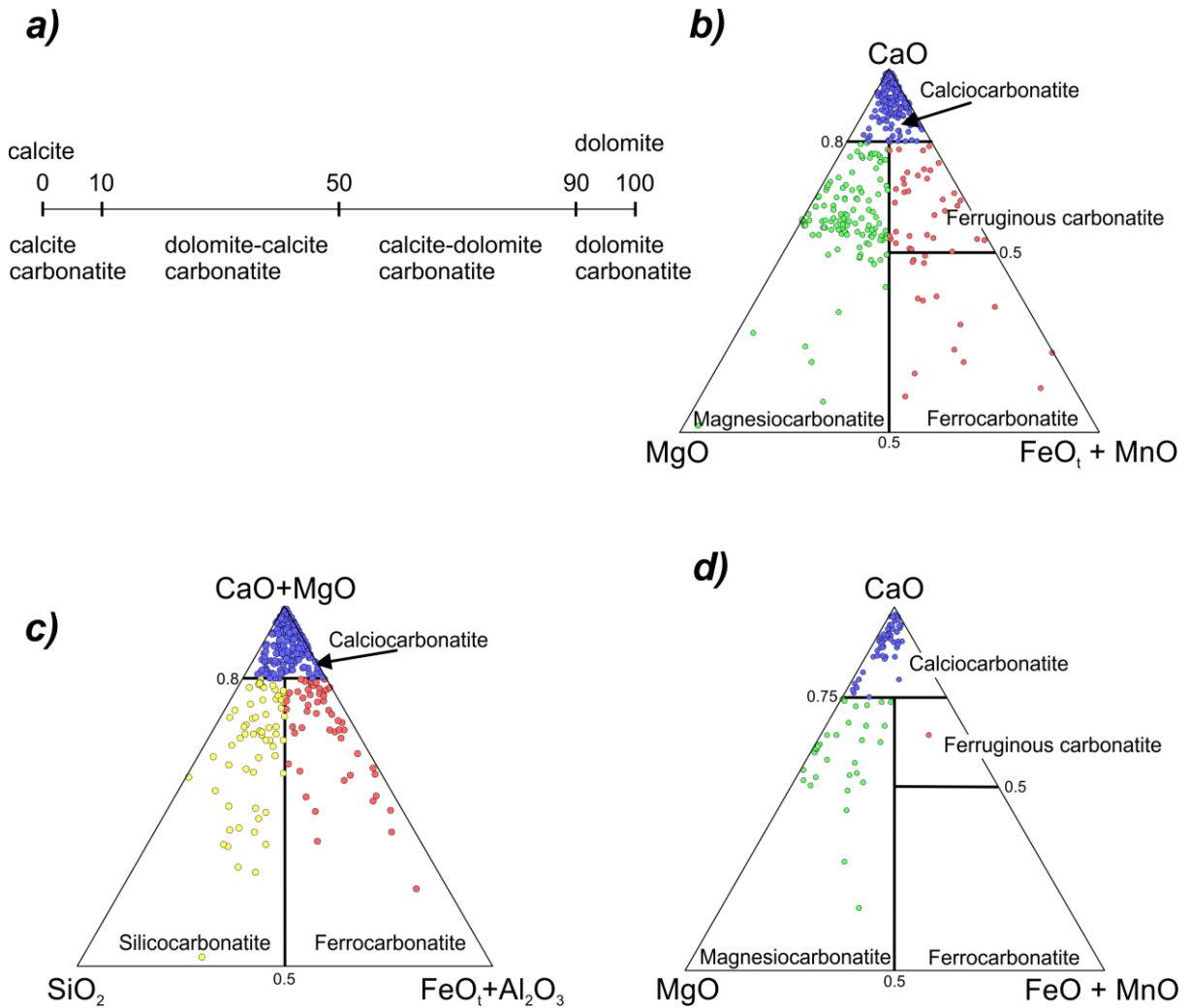


Fig. 1.2. Classification of global carbonatites dataset using a) binary representation defined by Streckisen (1974), b) MgO-CaO- $\text{FeO}_t + \text{MnO}$ ternary diagram (Le Maitre, 2002; Woolley, 1982), c) SiO₂-CaO- $\text{FeO} + \text{MnO}$ (Srivastava, 1993 from Mitchell and Gittins, 2022), d) molar ratios of MgO-CaO- $\text{FeO} + \text{MnO}$ (Gittins and Harmer, 1997). Data was compiled from

the GEOROC database (Digis, 2024; Sarbas and Nohl, 2008). *Note:* only one-third of carbonatites from the GEOROC database have the sole Fe^{2+} contents determined. Therefore, due to variable proportions of magnetite in carbonatites, the FeO should not be calculated from FeO_i without precisely knowing the amount of Fe^{3+} bearing minerals phases.

Nowadays, the origin of carbonatites is explained by the following three different processes:

- a) Partial melting of metasomatized CO_2 -rich mantle peridotite, eclogite, or pyroxenite (Dalton and Presnall, 1998; Dalton and Wood, 1993; Dasgupta et al., 2006; Ghosh et al., 2009; Hammouda, 2003; Harmer and Gittins, 1998; Wallace and Green, 1988; Wyllie and Lee, 1998; Ying et al., 2004)
- b) Progressive fractional crystallization of alkaline and SiO_2 -undersaturated magmas such as nephelinite, phonolite, lamproite, syenite, phoscorite, or kimberlite (Gittins, 1988; Lee and Wyllie, 1994; Nadeau et al., 2016; Veksler et al., 1998; Watkinson and Wyllie, 1971; Weidendorfer et al., 2016),
- c) Separation of carbonatite magma/liquid through the process of liquid immiscibility from notably silicate-deficient parental magmas (Brooker, 1998; Brooker and Kjarsgaard, 2011; Freestone and Hamilton, 1980; Kjarsgaard and Hamilton, 1988; Koster van Groos and Wyllie, 1966; Lee and Wyllie, 1997; Van Gross and Wyllie, 1963).

These processes are not mutually exclusive and petrogenesis of carbonatite melt/liquid can involve their combinations. Furthermore, all ongoing as well as final-stage melts/fluids can be further modified by additional fraction crystallization, reaction with wall rock and its assimilation as well as loss of alkalis during interaction with surrounding lithologies producing fenites (Yaxley et al., 2021). An idealized scheme with the possible paths of carbonatite magma origin is shown in Fig. 1.3.

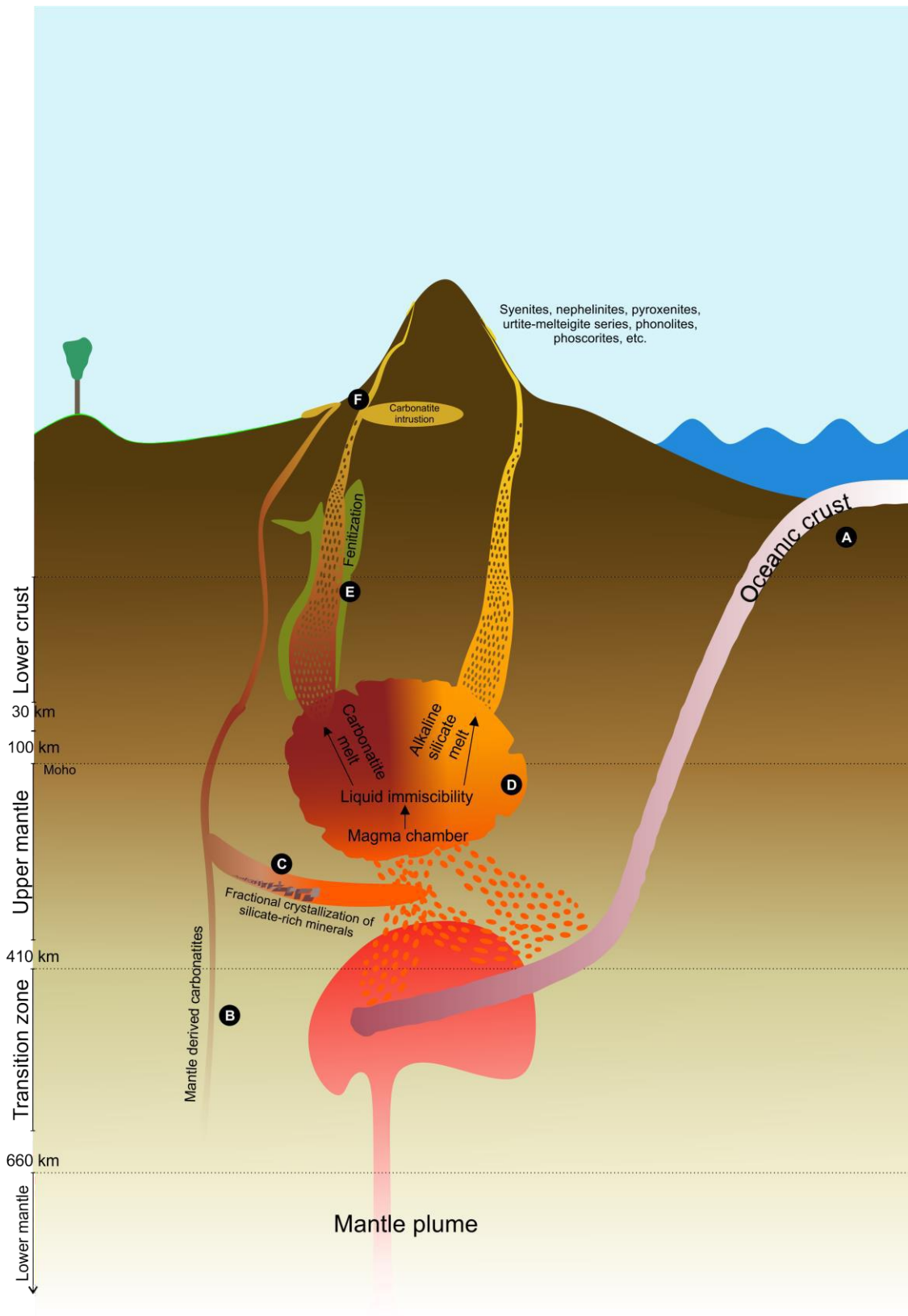
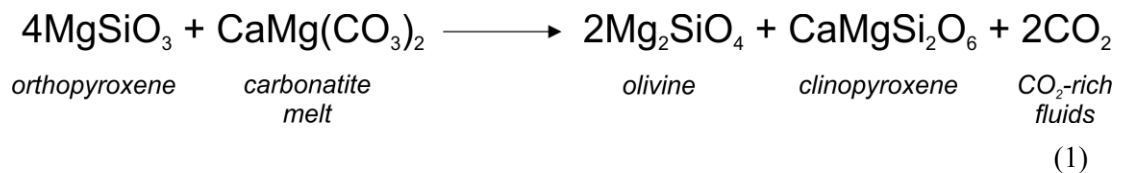


Fig. 1.3. A simplified and idealized model of deep carbon recycling and three possible mechanisms of carbonatite origin. A. subduction of oceanic crust into the mantle transition zone with associated addition of carbon from the oceanic sedimentary rocks (e.g., carbonate, evaporite); B. Mantle-derived carbonatites formed by partial melting of CO₂-rich mantle lithologies, C.

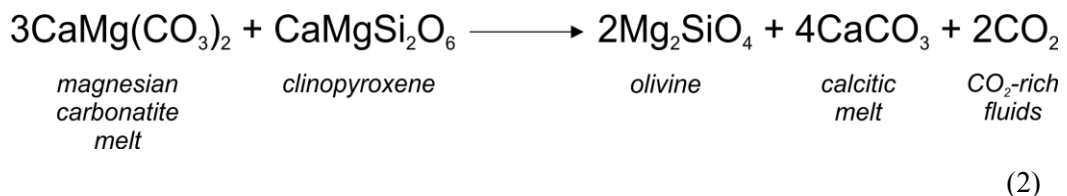
Fractional crystallization of silicate-rich minerals, namely olivine, clinopyroxene, nepheline, and others from the alkaline and SiO₂-undersaturated mantle-derived melt. At the same time, highly evolved, carbonate-rich melts enriched in REE can be produced, D. Segregation of carbonatitic melt from alkaline silicate melt by liquid immiscibility; E. During the ascent, carbonatite magma might interact with surrounding lithologies to form metasomatic fenites.; F. Eruption of carbonatitic magma on the surface, while this process is rather unlikely, and most carbonatitic melts crystallized at deep subsurface. Based and redrawn from Ackerman et al. (2021) and Yaxley et al. (2021, 2022).

1.2.1. Primary mantle-derived carbonatites & origin of magnesiocarbonatite

During mantle melting, first batches of magnesiocarbonatites may react with peridotitic orthopyroxene in the wall rock and produce olivine, clinopyroxene, and CO₂-rich fluids as described in equation (1). This reaction can modify peridotite mineralogy to the extent that the majority of orthopyroxene can be locally replaced by clinopyroxene-rich lithology represented by apatite-bearing wehrlite (Yaxley et al., 2021).



Later, magnesiocarbonatite batches will react with wall rock armored by wehrlite (an ultramafic rock predominantly consists of olivine and clinopyroxene) shifting carbonatite composition towards a more calcitic one as described in equation (2). This can be seen, for example, in Kerimasi calciocarbonatites in Tanzania where mineral phases are predicted to be in equilibrium with magnesiocarbonatite (Harmer and Gittins, 1997 and reference therein).



Carbonatites that are not associated with any alkaline silicate rocks and/or those carrying mantle xenoliths are considered to be primary mantle-derived rocks (Harmer and Gittins, 1997; Yaxley et al., 2021). This statement was supported by Gittins and Harmer (2003) who assume, based on petrology and geochemistry, that carbonatites from Dorowa, Shawa, Buhera, and Spitzkop,

represent primary partial melts. In these bodies, first erupted carbonatite magma is followed by silicate magma with no clear genetic relationship between each other and both magmas only appear to use the same conduits *en route* to the surface.

At first, it was assumed that magnesiocarbonatites (as well as ferrocarbonatites) are the product of low-temperature (sub-solidus) replacement of calcite or silicate minerals by dolomite (e.g., Barker, 1993) which would disqualify magnesiocarbonatite melts as primary melt. The field relationships, geological associations, frequent grain orientation during emplacement, and sheer volume of magnesiocarbonatite phase in carbonatite complexes in the Canadian and South African shield, respectively (e.g., Bulhoek, Shawa, Derdepoort, Spitskop, Seabrook Lake) where magnesiocarbonatites are dominant or even exclusive, however, are not consistent with the replacement theory (Harmer and Gittins, 1997). Besides, Newania carbonatite, India, is also dominated by magnesiocarbonatite and is considered to represent primary mantle-derived magma (Doroshkevich et al., 2010). Moreover, the conversion of CaCO_3 to almost pure MgCO_3 would require an enormous amount of magnesium exchanged in a ratio of 1:1 for calcium which is very unlikely. Furthermore, the same amount of calcium would therefore require extended space accommodation after the reaction forming late-stage Ca-rich lithologies around the carbonatite bodies that are not observed.

Liquid immiscibility, as a possible origin of magnesiocarbonatites, was ruled out by experiments done by Lee and Wyllie (1997, 1998) as the fractionation path of mantle peridotite derived melts would not intersect the miscibility gap. On the other hand, the idea of direct partial melting of the upper mantle as a main source of Mg-rich carbonatites is supported by numerous experimental works (e.g., Dalton and Wood, 1993; Harmer and Gittins, 1998; Wallace and Green, 1988; Ying et al., 2004). In this respect, the importance of carbon and other volatiles in the upper mantle is that they will largely reduce solidus temperature, and therefore, melting may occur several hundred °C below melting temperatures that are typical for silicate mantle-derived melts. Consequently, the carbonatitic melt is the first phase formed during partial melting (Dasgupta and Hirschmann, 2010). In the experimental work of Hunter and McKenzie (1989), the fraction of separated dolomitic melt was determined to be as low as 0.02%. At the same time, they calculated and measured the dihedral angle of a dolomitic melt in contact with olivine (the predominant mineral phase in the upper mantle; Jackson, 2000) which was set to 28° whereas the minimum dihedral angle required for interconnectivity of the fluids and matrix is 60°. This means that carbonatite with a dolomitic composition can migrate upwards and generate a network of melt/fluid along grain boundaries which is aided by the extremely low viscosity of carbonatite melt ($< 0.07 \text{ Pa s}$; compared to Etna alkali basaltic melts at $\sim 10 \text{ Pa s}$; Dobson et al., 1996; Giordano and Dingwell, 2003; Kono et al., 2014; Treiman and Schedl, 1983). This allows carbonatitic melt to efficiently migrate through the Earth's upper mantle, but also within crustal lithologies. These first melts would be greatly enriched in

many incompatible elements such as large-ion lithophile elements (LILE; e.g., Sr, Ba), REE that are strongly partitioned into carbonatitic melts as shown for example in Adam and Green (2001) where partitioning coefficients between mantle minerals (such as clinopyroxene, amphibole or garnet) and carbonatite melt are almost exclusively <1 reaching ratios up to 0.001. Direct evidence for the origin of carbonatitic magmas in the upper mantle conditions was presented by Lee and Wyllie (1998) showing that the carbonate-rich magmas can be generated by partial melting of dolomite–magnesite-rich peridotite at depths greater than 70 km. In this respect, the Sisimiut-Maniitsoq magnesiocarbonatite dike swarm in Sarfartoq, Greenland, was interpreted by Mitchell et al. (1999) to represent a primary, mantle-derived partial melting-related sequence. Similarly, the Newania magnesiocarbonatite complex is also considered to be primary mantle-derived because it is not related to any alkaline silicate rocks (Mitchell, 2005). This statement is supported by stable isotope composition (Ray et al., 2010) as well as petrography and Nb/Ta systematics (Ray et al., 2013). If magnesiocarbonatite reaches the crust it may start to precipitate calcite or dolomite if the temperature is not high enough to avoid dissociation of dolomite (Harmer and Gittins, 1997).

If magnesiocarbonatitic melts truly originated in the mantle conditions, then the majority of them should be displayed in the top left quadrant (I) of $\epsilon_{\text{Sr}}(\text{i})$ – $\epsilon_{\text{Nd}}(\text{i})$ plot (Fig. 1.4), a feature that is characteristic of mantle-derived melts. However, the analyses of global data from the GEOROC database show that only ~40 % of samples have Sr–Nd isotopic composition similar to that of the mantle (compared to calciocarbonatite where ~50 % of samples fall into the quadrant I). This dichotomy can be explained by several possibilities: **(1)** magnesiocarbonatites do not represent primary mantle-derived melt as assumed above and/or **(2)** more than a half of global magnesiocarbonatites have been somehow modified during their transport. However, I note that carbonatites should be, in principle, more resilient to contamination in terms of Sr and Nd because of their typically very high Sr–Nd contents. Indeed, magnesiocarbonatites displayed in the first quadrant have higher concentrations of Sr (~ 60 %) and Nd (~ 20 %) than other samples shown, which might argue for their preserved isotopic composition. Nonetheless, even samples occurring outside the mantle $\epsilon_{\text{Sr}}(\text{i})$ – $\epsilon_{\text{Nd}}(\text{i})$ region exceed the Sr–Nd concentrations typical for crustal lithologies (about 10 times). Finally, it is equally possible **(3)** that the rock classification of magnesiocarbonatite based on bulk-rock MgO–CaO–FeO_T+MnO composition (Le Maitre, 2002; Woolley, 1982) is simply incorrect for the reasons described above.

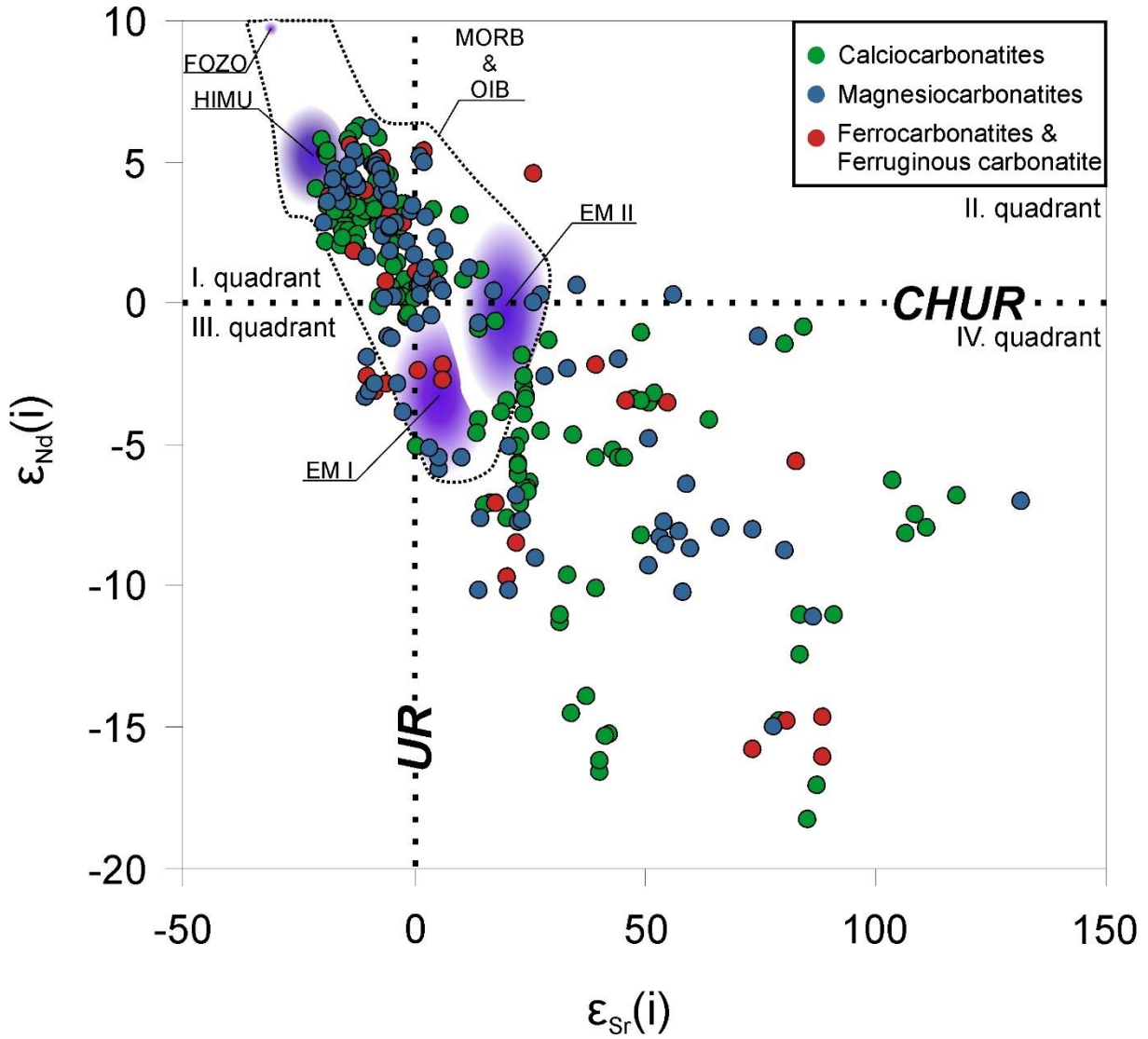


Fig. 1.4. The global $\epsilon_{\text{Sr}}(i)$ - $\epsilon_{\text{Nd}}(i)$ compositions of the three main carbonatite types. Note that the majority of carbonatites are presented in the top left quadrant, which might imply their primary mantle-derived origin. Data from the GEOROC database (Digis, 2024; Sarbas and Nohl, 2008). Mantle reservoirs redrawn from Harmer and Gittins (1998) with data used from Hofmann (1997) for HIMU, EM I, EM II, MORB, and OIB reservoir and Hart et al. (1992) as reference for FOZO.

1.2.2. Liquid immiscibility, carbonatite-silicate rock association & origin of calcio/ferro carbonatites

As exemplified in Fig. 1.3, field observations indicate a close relationship of carbonatites with alkaline igneous rocks such as lamprophyres, nephelinites, urtite–melteigite series (urtite, melteigite, ijolite, foyaite), syenites, or melilites (e.g., Bell, 1998). In fact, the co-occurrence rate is very high, about 74% (Yaxley et al., 2021), and together with the intimate textures, these collective lines of the evidence might indicate that the majority of calciocarbonatites have originated through liquid immiscibility from highly fractionated alkaline silicate melts, as a cumulate rock crystallized from calcite–dolomite

melt or by pronounced fractionation of CO₂-rich silicate melts (Yaxley et al., 2022). Le Bas (1981) or Dawson (1993) suggested that some calciocarbonatites are products of the loss of alkalis (finitization) from originally natrocarbonatitic magmas with a composition similar to those in Oldoinyo Lengai. However, Lee and Wyllie (1998) argued that based on the phase equilibrium modeled in the range of pressure 1.0–2.5 GPa (lower crust to upper mantle), immiscible calciocarbonatite magmas should contain at least 10 wt. % of (Na,K)₂CO₃ and less than 80 wt. % of CaCO₃. This is supported by the study of Berndt and Klemme (2022) who described coexisting blebs of carbonate–silicate liquids in haüyne-hosted melt inclusion from the Laacher See phonolitic volcano, Germany. Similarly, Guzmics et al. (2011) and Káldos et al. (2015) described melt inclusions in alkali-rich Kerimasi (neighboring to Oldoinyo Lengai) calciocarbonatites where parental melt started to crystallize both silicate (forsterite) and carbonate (calcite) minerals. With progressive crystallization of olivine, apatite, and magnetite the carbonatitic melt will leave the miscibility gap (Fig. 1.5.), and during the later crystallization of calcite, the composition of the remaining melt will shift towards the more alkaline one approaching the composition of natrocarbonatite. In Shombole nephelinites, Kenya, ≤ 0.5 cm large globules of carbonatite quenched melt that contains zeolite, fluorite, strontianite, and fluorapatite were found. Such mineral assemblage and composition were nearly identical to the silicate groundmass and are therefore considered to represent the product of liquid immiscibility (Kjarsgaard and Peterson, 1991). Another example that supports the model of liquid immiscibility was presented by Halama et al. (2005) from the Grønnedal-Ika carbonatite complex using oxygen fugacity estimates, REE patterns, and ε_{Nd} values. Nevertheless, it is important to note that experiments of Brooker and Kjarsgaard (2011) suggest that slightly alkaline carbonatites could be produced by liquid immiscibility only at crustal conditions. Therefore, they ruled out the possibility of liquid immiscibility occurring in the mantle due to the high CO₂ solubility in the silicate melt at high pressures (e.g., Blank and Brooker, 1994; Mysen and Virgo, 1980). Kjarsgaard and Hamilton (1988) suggest that the common sequence of alkaline silicate rocks (melilite – ijolite – urtite – phonolite) being associated with carbonatite complexes represent the product of parental magma. Moreover, with more progressive fractionation and mineral crystallization, the resulting carbonatitic melt is closer to the composition of natrocarbonatite. The suggested evolution of natrocarbonatites is displayed in Fig. 1.5. However, this observation contrasts with that presented by Le Bas (1981) and Dawson (1993).

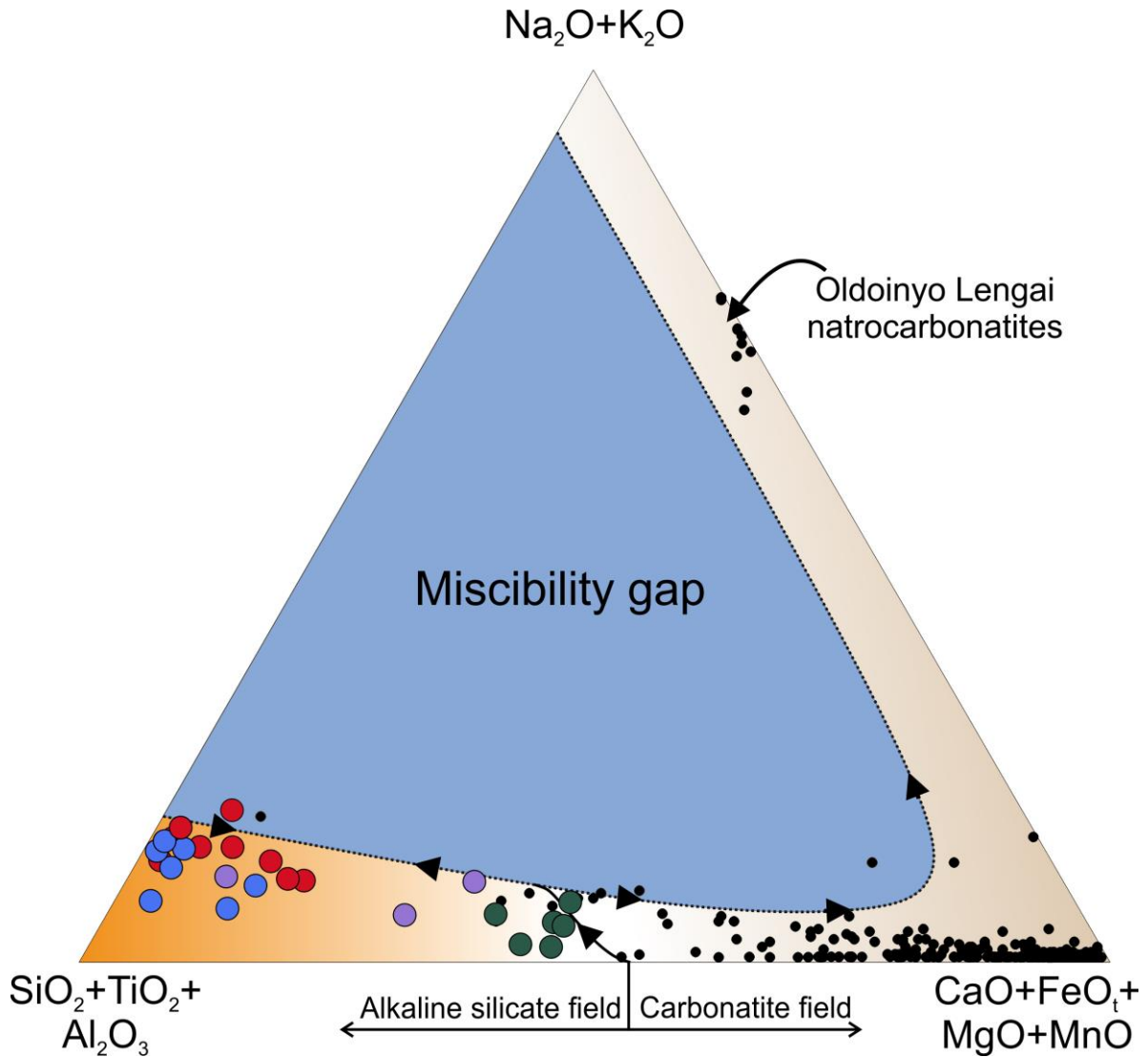


Fig. 1.5. Ternary plot of $\text{SiO}_2+\text{TiO}_2+\text{Al}_2\text{O}_3 - \text{Na}_2\text{O}+\text{K}_2\text{O} - \text{CaO}+\text{FeO}_t+\text{MgO}+\text{MnO}$ for global carbonatites included in the GEOROC database (Digis, 2024; Sarbas and Nohl, 2008) and alkaline silicate rocks closely linked with Tamil Nadu carbonatites (Ackerman et al., 2019, 2017). Projection based on Berndt and Klemme (2022) and Hamilton et al. (1979). Black – carbonatite, green – pyroxenite, purple – gabbro, red – syenite, blue – tonalite, and monzonite, arrows indicate cooling direction. Note, that the size and shape of the miscibility gap can change with variable temperature, pressure, and/or the contents of P_2O_5 , H_2O , and F.

To summarize, a prevalent number of studies highlight the fact that the origin of the majority of calciocarbonatites linked with alkaline silicate volcanism/magmatism is closely connected with the processes of liquid immiscibility and, therefore, those calciocarbonatites cannot be considered as a primary mantle-derived melts. Indeed, no natural evidence of rapidly quenched calcitic or dolomitic melts that would represent either primary or derivative magmas has been found so far (Mitchell, 2005) while recent observations at the Kaiserstuhl volcano, Germany, provided evidence for possible

calciocarbonatite melts quenched at the surface or shallow subsurface (Rapprich et al., 2024). Yet, while calciocarbonatites are probably not primary mantle-derived melts, they carry a strong mantle signature in case of stable and radiogenic isotopic composition (see more details in Chapters 1.5 – 1.9).

To further complicate the calciocarbonatite paradigm, another explanation of their origin is also crystallization from primary magnesiocarbonatitic melt. This idea is supported by the experimental work of Harmer and Gittins (1997) where calcite–fluorite cumulate was recognized at the base of the experimental charge and also by some field observations when some calciocarbonatites were found with marked cumulate textures (e.g., Dicker Willem carbonatite complex, southwest Namibia; Cooper and Reid, 1991). Also, I note that calcite is capable of crystallizing over a large range of temperatures starting at least at 300 °C (Tolley, 2018 and references therein). This newly formed calcite and apatite will start to accumulate and the removal of CaO might shift the melt composition towards a more alkali composition while the first crystals of nyerereite $[\text{Na}_2\text{Ca}(\text{CO}_3)_2]$ will begin to crystallize. However, considering that most of the calciocarbonatites lack cumulate texture, this process should be overall considered as rather uncommon in nature.

Ferrocarbonatites representing a rather minor carbonatite lithology are most likely produced by multistage processes involving late-stage overprint of former carbonatite lithologies by carbonate- and chloride-rich hydrothermal fluids and/or pervasive fenitization of country rock (Yaxley et al., 2021). In fact, ferrocarbonatites are often linked with late-stage hydrothermal activity sometimes expressed by e.g., Ba–F mineralization as in the case of Amba Dongar in west India and Central Tuva in southern Siberia (Prokopyev et al., 2016; Viladkar, 2018). An alternative explanation of ferrocarbonatite formation is the petrogenetic model proposed by Chandra et al. (2019) claiming that the Amba Dongar ferrocarbonatites represent the products of secondary melting of previously solidified carbonatite veins originated by low-degree partial melting of metasomatized subcontinental lithospheric mantle (SCLM). Fractional crystallization from carbonatite melt as one of the possibilities of ferrocarbonatite formation is mentioned in Kjarsgaard and Hamilton (1988). On the other hand, Thompson et al. (2002) suggested that, based on stable and radiogenic isotopic compositions, the Swartbooisdrif ferrocarbonatite, Namibia, represents a former mantle-derived melt that was not largely modified during its route to the surface by e.g., crustal contamination and/or late-stage alteration. Similarly, calcium isotopic systematics (expressed as $\delta^{44/42}\text{Ca}$; see in more details in Chapter 1.5.2.) attests for a mantle origin of ferrocarbonatites from Belaya Zima, Russia, because fractionation of calciocarbonatite melt would shift ferrocarbonatite melt to isotopically lighter composition, which was not observed. However, the collective evidence gathered so far (common mineral assemblage typical for fractional processes, enrichment in REE and other incompatible elements, stable/radiogenic isotopic compositions, field relationship evidence, etc.) suggests that most ferrocarbonatites and ferruginous carbonatites cannot be considered as a primary derived melts or only at extreme cases.

To summarize, all of the above-mentioned mechanisms of carbonatite origin have to be approached with respect to the detailed petrography and geochemistry of the specific carbonatite site. There is no reason to expect that all types of carbonatites have a uniform pattern of formation but rather, a combination of P – T – X – f conditions and their surroundings *en route* to shallow levels interplay in their petrogenesis. Thus, each carbonatite complex requires a critical evaluation of collected petrological and geochemical data to make a proper interpretation of its formation and evolution.

1.3. Economic and global significance

There are worldwide ~ 600 reported carbonatite occurrences in total and ca. 50 of them have been either actively or historically mined for several critical metals which makes carbonatites one of the most mined lithologies with respect to their rather rare occurrence. This is because carbonatitic melts have unique chemical and physical properties that allow them to accumulate large amounts of rare earth elements (REE), especially light rare earth elements (LREE; La, Ce, Pr, Nd, Sm, and Eu) as well as other incompatible elements Nb, Th, U, P, Sr, and Ba (Gittins, 1988) that are typically presented in very low contents in silicate-dominated lithologies. Since there is very high demand for these elements that are commonly used as catalysts, medical tracers, in high-end technology like optical lenses, super-strong magnets, or as a part of control rods in nuclear reactors (Goonan, 2011), this makes carbonatites one of the most important targets of supply worldwide.

Characteristic enrichment of REE and typically predominance of LREE over HREE (heavy rare earth elements; Tb, Dy, Ho, Er, Tm, Yb, and Lu) in carbonatites can be best explained by: **(1)** low-degree partial melting of parental carbonatitic melts where large ionic radii of LREE ensure more incompatible behavior than HREE and, therefore, LREE will preferentially partition into the melt phase and HREE will remain in the residue (Winter, 2014), **(2)** collective presence of REE-bearing minerals in large quantities in carbonatites (monazite, apatite, strontianite, parasite, bastnäesite, synchysite, ancylite, xenotime; Beland and Williams-Jones, 2021), **(3)** the prevailing low silica content of carbonatitic melts can trap REE in early crystallizing apatite (Anenburg et al., 2020), **(4)** late-stage enrichment of REE in response to extensive fractional crystallization (Broom-Fendley et al., 2017), and **(5)** REE enrichment by secondary post-emplacement hydrothermal processes (Wang et al., 2020) and by weathering processes (Gupta and Krishnamurthy, 1992).

Carbonatites represent the most dominant source of REE worldwide (Goodenough et al., 2016; Jackson and Christiansen, 1993), especially LREE. The largest currently exploited REE deposit is the Bayan Obo carbonatite site (Weng et al., 2015). Here, the main body of REE–Nb–Fe deposit reaches an average REO (sum of rare earth element oxides) content of up to 6.19 wt.% (Gupta and Krishnamurthy, 1992) and contains ~57.4 Mt REO (~30% of worldwide supplies; Gómez-Arias et al.,

2022; Weng et al., 2015). Yet, the highest grade of REO can be found in the Mount Weld carbonatite site in Australia reaching up to 26.1% REO (Gupta and Krishnamurthy, 1992). However, the minable contents of REE are not always directly linked to the minerals in carbonatite, but sometimes rather to spatially and temporally associated silicate alkaline rocks. For example, Schiel in South Africa is the main source of REE-fluorapatite in pyroxenites and phoscorites, whereas allanite and titanite occur predominantly in syenites (Graupner et al., 2018). Overall, carbonatites carry more than half of the global REO inventory (Fig. 1.6.; Weng et al., 2015), whereby China accounts for an estimated 70 % of global production in 2022 (Andrews-Speed and Hove, 2023) and is responsible almost for 90 % of REE refining (IEA, 2021).

In June 2024, the Rare Earths Norway (REN) group presented the results of three years of exploration of Fen Carbonatite Complex, Vestfold, and Telemark region, which is also included in this thesis as one of the studied sites targeted for its isotopic signatures (see Chapter 2). Here, the REE contents of calciocarbonatites range from ~740 to 14,000 ppm while analyzed magnesiocarbonatite yields around 1.35 wt.% and rödberg has ~1.4 wt.% (~1.62 wt.% of total REO). These results add to the previous REN report where 1.57 wt.% (1.54 wt.% LREO) of total REO was detected, which means that the now determined REE reserves (120 Mt; Weng et al., 2015; Fig 1.6) have been grown by additional 8.8 Mt. Thus, the Fen Carbonatite Complex is currently the largest rare earth element deposit in Europe (Norway, 2024).

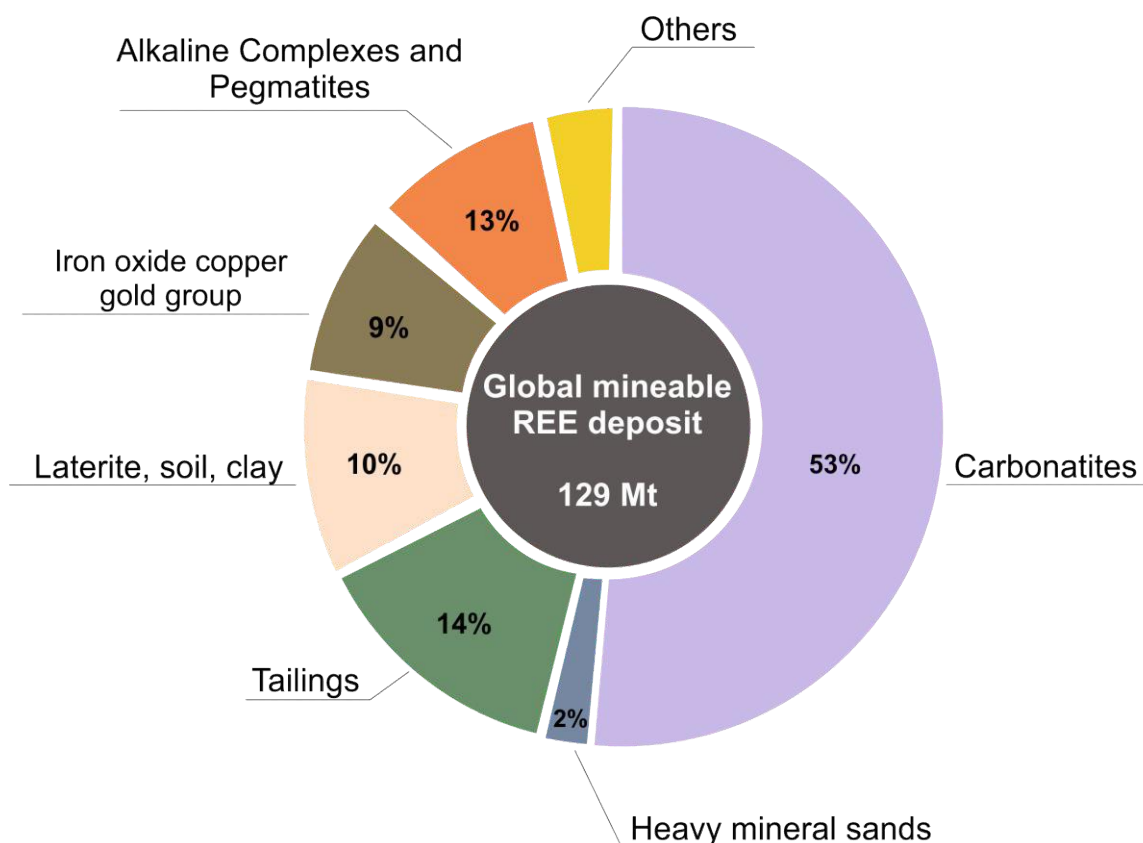


Fig. 1.6. Percentage representation diagram of the deposits currently mined for REE with respect to principal deposit type. Redrawn from Weng et al. (2015) and complemented by a newly discovered REE deposit in Fen Carbonatite Complex, Norway.

Another critical element obtainable mainly from carbonatites is Nb, which is widely used in catalytic applications, medical implants, and battery alloys, but mainly as a microalloying element added to the steels. Such alloys can significantly improve the strength, toughness, weldability, weight reduction, and resistance to corrosion (Heisterkamp and Carneiro, 2001). Niobium is extracted from pyrochlore and perovskite group mineral phases that are characteristic of many carbonatites and associated phoscorites (Mitchell, 2015). About 92% of the current global production of Nb comes from Alto Paranaíba Igneous Province in Brazil (Velásquez-Ruiz et al., 2024).

Finally, carbonatites and related alkaline rocks were in the past or are currently also mined for some non-critical metals like Cu in Phalaborwa, South Africa, with Au, Ag, and Pt being represent byproducts (Palabora Mining Company, Ltd., 1976). Also, sulfides, as well as Zn, Cu (Grenne et al., 1999), and Fe (Ihlen et al., 2014), were mined in Scandinavian carbonatites until the 90' and U and Ti in the Caldaws Alkaline Massif, Brazil (Ulbrich et al., 2005). Among other industrial minerals, fluorite was mined in Amba Dongar, India (Viladkar, 2018), and phosphate in Kovdor, Russia (Krasnova et al., 2004b). Fenites, as products of carbonatite metasomatism, can also be mined for several elements,

such as Fe, Cu, Ti, Th, U, and fluorite. In fact, some of them were mined since 770 AD (Elliott et al., 2018 and references therein).

Nowadays, there is strong pressure on mining companies to fulfill the highest requirements to protect the environment more than before and, therefore, reduce SO₂ emissions from smelting. Sulfuric acid, a by-product of the smelting process, can be reacted with carbonatite-derived apatite and disposed of as superphosphate fertilizer (Cantin et al., 1999; Gittins, 1988). Metals acquired from carbonatites indirectly contribute to the reduction of CO₂ emissions by their integration into the technology-producing energy (e.g., advanced steel alloys, Mohrbacher, 2015).

1.4. Assisted fenitization & carbonatite alteration

Carbonatitic magmas can undergo a series of modifications starting with magmatic, sub-solidus metasomatic processes, continuing through carbo-hydrothermal and hydrothermal changes, and ending by late-stage alteration, the latter being recognized by detailed petrography and geochemical studies (Yaxley et al., 2021). Additionally, carbonatites are extraordinarily prone to weathering if they reach surface conditions as well as chemical exchange with their surroundings during emplacement at the shallow levels in the crust followed by extensive re-equilibration. This susceptibility is caused by high concentrations of volatiles (CO₂ and H₂O) in their parental melts, large physicochemical differences between commonly occurring minerals in carbonatites and surrounding lithologies, and relative solubility of carbonate minerals in the water boosted by even slightly acidic environment. For all these reasons, it is believed that the majority of carbonatites undergo an alteration to some extent (Chakhmouradian et al., 2016). A secondary chemical manifestation in carbonatites is very briefly described below.

The most important rock transformation that are carbonatitic magmas responsible for is fenitization which has been used by mining prospectors for decades as a possible indicator of economically valuable mineral deposits associated with carbonatites and alkaline igneous complexes. Fenitization is a transformation of country rock by contact metasomatism during the cooling and crystallization of carbonatitic magmas and/or or carbonated alkaline melts (Le Bas, 2008). The assisted rock transformation caused by fenitization commonly changes the chemical rock composition in the distance starting at several centimeters and reaching up to several kilometers (Elliott et al., 2018) from the carbonatite melt/fluid conduit. The fenitization typically causes an overall enrichment by selected incompatible trace elements (e.g., alkalis, high-field strength elements such as Nb, U or Th, and fluid-mobile elements such as Sr, Ba) advantaging their enhanced solubility in complexing ligand forms (as chloride, fluoride, sulfate, phosphate, and carbonate anions; Elliott et al., 2018 and references therein). Since these elements exhibit different degrees of mobility at certain conditions with respect to e.g., P–T conditions, their co-variation can be used for the carbonatite and fenite

petrogenesis. For example, potassium is considered to be more mobile compared to Na and therefore, it is transported at lower depths while forming potassic fenites. In comparison, sodium has been preferentially lost from carbonatitic melts at deeper depths while temperatures are $> 600\text{ }^{\circ}\text{C}$, forming earlier and deeper-seated sodic fenites (Elliott et al., 2018; Yaxley et al., 2022). Due to the sometimes extensive fenitization of country rocks, the fenites became a powerful and effective exploration rock indicator that is sometimes mined directly for several critical and non-critical elements.

The late-stage sulfide mineralization is sometimes present in carbonatites (e.g., Fen Complex, see Chapter 4; Polák et al., in press), mostly expressed by the occurrence of pyrite can be recognized by the detailed petrographic studies (e.g., presence of large pyrite grains with euhedral shapes, sulfides filling late-stage fractures, etc.) since the primary sulfides representing the products of crystallization of late-stage sulfur-rich melt/fluid are usually represented by globular phases being enclosed in carbonate minerals and/or trapped in the carbonated melt inclusions (e.g., Guzmics et al., 2012). In terms of secondary molybdenite, its presence can be easily detected by excessive concentrations of Re that are positively correlated with S suggesting crystallization from sulfur-bearing hydrothermal solutions (see Chapter 4). Another common alteration process detected in carbonatites is extensive hematitization which is especially characteristic for ferrocarbonatites and their altered rock type called rödberg. During this alteration, a conversion of iron-bearing carbonates and oxides (e.g., magnetite, ankerite, ilmenite) happens, and carbonatites become more fragile, and porous serving as an efficient trap for some late-stage hydrothermal fluids percolating through the rock giving rise to some extremely anomalous concentrations in certain elements such as Th or U. For example, the single rödberg sampled at the Fen carbonatite complex (CFN 7) exhibit severe enrichment in Th (1,570 ppm, Supplementary material in Chapter 3) and may, therefore, pose a health risk to local residents and nature.

In unaltered carbonatites, REE and Sr with Ba are predominantly hosted in calcite and fluorapatite. In contrast, during the late-stage carbo-hydrothermal and hydrothermal alteration, these REE-bearing minerals recrystallized to minerals like Ce-parisite, baryte, strontianite, celestinite, and also economically important pyrochlore (Cangelosi et al., 2020) with respect to nature and composition of percolated hydrothermal solution. During these processes, REE may be largely mobile and over-concentrated in hydrothermal fluids, and, therefore, remarkable REE deposits have been reported near carbonatites (e.g., Anenburg et al., 2020). Whether these transformations can have a significant impact on e.g., isotopic systematics has been a matter of debate. In this respect, my data from the e.g., Iron Hill carbonatites (USA) indicate that when comparing two similar samples, the more altered (UC 17B), and the less altered (UC 17A) samples, the bulk-rock Sr isotopic compositions seem to remain unchanged (Chapter 2).

1.5. Unravelling the source and evolution of carbonatites through isotope systematics

The exact nature of sources parental to carbonatitic magmas remains the subject of debate for decades (see e.g., Gittins, 1988; Gittins and Mitchell, 2023; Mitchell and Gittins, 2022; Yaxley et al., 2022 and references therein) For example, based on Sr–Nd–Pb compositions, many authors attribute the source of carbonatite origin to either HIMU (high $^{238}\text{U}/^{204}\text{Pb} \equiv \mu$; low $^{87}\text{Sr}/^{86}\text{Sr}$ and high $^{206}\text{Pb}/^{204}\text{Pb}$), FOZO (Focal zone; relatively high $^{206}\text{Pb}/^{204}\text{Pb}$), EM I (Enriched mantle I; low $^{143}\text{Nd}/^{144}\text{Nd}$ and high $^{87}\text{Sr}/^{86}\text{Sr}$), EM II (Enriched mantle II; high $^{87}\text{Sr}/^{86}\text{Sr}$), or even DMM (depleted MORB mantle; low $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$) sources and/or suggested their different contribution (e.g., Harmer and Gittins, 1998; Simonetti and Bell, 1994; Tilton and Bell, 1994; Yaxley et al., 2021; Fig 1.5.). However, while establishing which samples lie in close vicinity or between the above-mentioned source regions is rather an easy task for young carbonatites, it became sometimes problematic for the Precambrian carbonatites with respect to sometimes enhanced alteration, uncertain ages, etc. As I show in Fig. 1.4 and 1.7, most of the carbonatites plot in the first quadrant in Sr–Nd space either on and/or close to the so-called mantle array attributed to mantle-derived melts with variable contribution of enriched mantle end-members. Yet, about ~30 % of global carbonatites do not essential plot to any of the above-mentioned mantle reservoirs and only a small proportion of them can be explained by some parental melt modifications or a source contamination, and this phenomenon is further discussed in sections 1.6 and Chapter 2. Also, as demonstrated in Fig. 1.7, the temporal distribution of carbonatites with respect to their $\varepsilon_{\text{Sr}}(\text{i})$ – $\varepsilon_{\text{Nd}}(\text{i})$ co-variation is non-systematic and therefore, does not represent the isotopic evolution of primary derived parental melts.

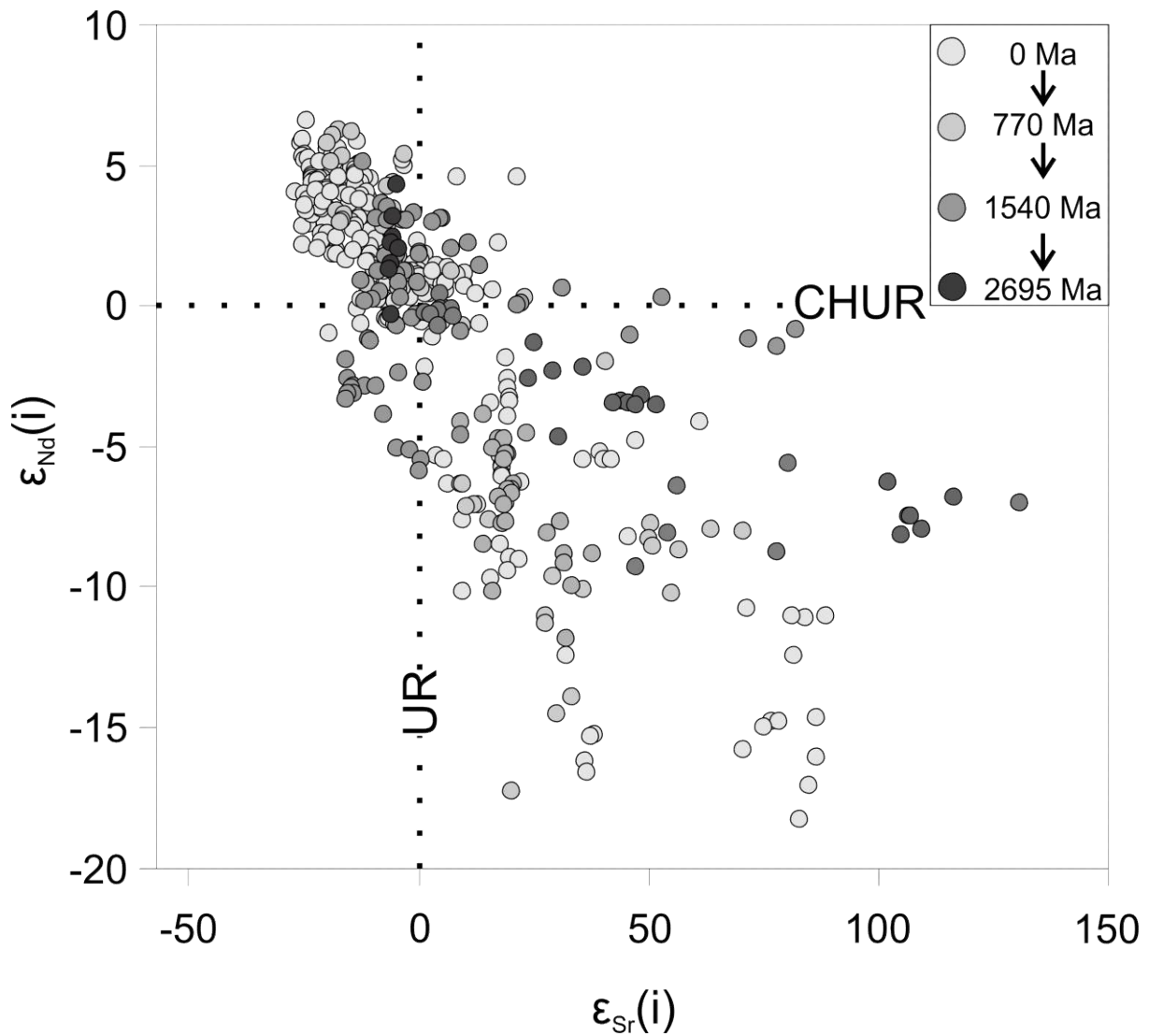


Fig. 1.7. A distribution of global carbonatite occurrence in terms of their initial $\epsilon_{Sr}(i)$ – $\epsilon_{Nd}(i)$ diagram with respect to their age. The older the samples the darker the color they pose.

1.5.1. Traditional stable isotopes: carbon, oxygen and sulfur

Carbonatites contain, by their nature, a number of volatile components, such as chlorine or hydrogen, that are sometimes used to investigate the evolution of a volatile inventory of carbonatitic melts/fluids (e.g., Eggenkamp and Koster Van Groos, 1997, Demény et al., 1998), but, naturally, two elements are characteristic for carbonatites – carbon and oxygen.

Carbon isotope composition is mostly expressed as the difference in $^{13}C/^{12}C$ between an unknown sample and established reference material, conventionally V-PDB (Vienna PeeDee Belemnite; Craig, 1957), at per mil scale:

$$\delta^{13}\text{C} (\text{‰}) = \left[\left(\frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}}{{}^{13}\text{C}/{}^{12}\text{C}_{\text{V-PDB}}} \right) - 1 \right] \times 1,000 \quad (3)$$

A similar approach has been used for oxygen isotope values where the difference between measured sample $^{18}\text{O}/^{16}\text{O}$ (and recently also $^{17}\text{O}/^{16}\text{O}$; Pack et al., 2016) and international reference material (V-SMOW, Vienna Standard Mean Ocean Water, Coplen, 1994) is accessed:

$$\delta^{18}\text{O} (\text{‰}) = \left[\left(\frac{{}^{18}\text{O}/{}^{16}\text{O}_{\text{sample}}}{{}^{18}\text{O}/{}^{16}\text{O}_{\text{V-SMOW}}} \right) - 1 \right] \times 1,000 \quad (4)$$

Knowledge of the carbon cycle is essential for understanding the Earth's history, distribution of hydrocarbons, prediction of geological hazards associated with volcanic eruptions as well as climate changes in the past (impact of greenhouse gases). The Earth's mantle contains $\sim 1\text{--}12 \times 10^{23}$ g carbon (Dasgupta and Hirschmann, 2010), hosted mainly in the accessory phases which change with increasing depth from CO_2 -bearing fluids, melts $\rightarrow$ calcite/dolomite $\rightarrow$ magnesite $\rightarrow$ diamond, and/or Fe-metal carbides (Dasgupta and Hirschmann, 2010). Yaxley et al. (2019) argued that carbonatitic melts are not stable at depths greater than 150–300 km, depending on $f\text{O}_2$ conditions, carbon concentrations, and mantle metal saturation. In fact, the mantle is proposed to be the main buffer of long-term deep carbon storage and budget. The carbon cycle in the mantle is controlled on the input side, by the subduction of oceanic plates with their sedimentary cover containing carbonates and other carbon-bearing rock such as organic-rich black shales (Brenker et al., 2007), and on the output side, by degassing of mantle-derived, CO_2 -bearing melts which are responsible for carbon release from the Earth's mantle (Yaxley et al., 2019). In this respect, there has been a steady increase in the number of occurrences of carbonatite since subduction processes operated at a great extent while rather few carbonatite bodies are older than ~ 2.5 Ga (the oldest known carbonatite intrusion is Tupertalik, Greenland, with an age of 3007 Ma; Bizzarro et al., 2002). This might be because of limited sources of shallow/surface carbon that could be introduced to sufficient depths at that time. One of the sources of primary carbon is primordial carbon, i.e. carbon presented in the Earth's mantle since its accretion, and carbon entrapped in carbonaceous meteorites delivered especially during Late Heavy Bombardment (~ 4 Ga) with an estimated about 3×10^{23} g of material corresponding to $\sim 0.005\%$ of Earth's mass (Kring and Cohen, 2002).

On the other hand, experimental works suggest that the depth limit for subducted carbonates is approximately 300 km while about 70 % of subducted carbonate can bypass the arc region and be incorporated into the mantle (Hammouda, 2003). Another evidence that the source of carbon in the

mantle could be represented by recycled material (see also Barker, 1996) was given by e.g., Woodard and Huhma (2015) whose studied carbonatites from Naantali, Finland (age of 1796 ± 9 Ma), and reported largely negative $\delta^{13}\text{C}$ signatures ($\sim -11\text{‰}$) characteristic for recycled carbon. Similarly, diamonds containing organic carbon with isotopic composition suggesting its formation in surface/shallow conditions, were also reported (Kirkley et al., 1991). Likewise, carbon with predominantly low $^{13}\text{C}/^{12}\text{C}$ ratios has been found in carbonatites from Fort Portal, Uganda (Deines and Gold, 1973) but such low ratios may not necessarily indicate recycled organic carbon. Instead, an alternative explanation may be late-stage re-equilibration by vegetation cover incorporated into the carbonatite tephra during a volcano landslide (Rapprich et al., 2024).

Oxygen isotopic compositions of igneous rocks are also commonly used to trace the nature of magma source as well as the evolution of parental magmas during the ascent to the surface including oxygen isotopic exchange among crystallizing minerals and/or possible addition of subducted fluids with commonly heavy $\delta^{18}\text{O}$ signatures (Bindeman and Pack, 2021; Taylor, 1968). In carbonatite research, when combined with carbon isotope compositions, they provide a powerful bi-isotopic tool to evaluate the nature of carbonatite source, the extent of hydrothermal alteration, or interactions with meteoric water. A brief compilation of proposed C–O isotopic paths applicable to carbonatite petrogenesis, together with the processes influencing stable isotope systematics, are shown in Fig. 1.8. The most plausible process that might shift the isotopic compositions of C, O, and S of primary magmatic rocks is (1) recycling of subducted oceanic or continental crust with sedimentary cover into deeper parts of mantle (Hoefs, 2009) or (2) contamination of primary magmas by sedimentary crustal material during a magma ascend which usually increase $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. Primary unaltered carbonatites have usually $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values between +5 and +15 and between -9 and -1 , respectively (compiled from Keller and Hoefs, 1995; Ray and Ramesh, 2006; Taylor et al., 1967). During mantle partial melting, the volatiles will preferentially enter the melt and then will be impoverished by e.g., magma degassing, which is often linked with isotopic fractionation. However, Keller and Hoefs (1995) and references therein assume that the fractionation of carbon isotopes between CO_2 and CaCO_3 is rather small, and therefore degassing of CO_2 should have only a minor impact on primary $\delta^{13}\text{C}$ values. In terms of oxygen isotopes, Muehlenbachs and Byerly (1982) revealed that the majority of Galapagos differentiated rocks show a difference in $\delta^{18}\text{O}$ only by 1.2 ‰ suggesting that magma differentiation does not play a major role in oxygen isotope fractionation.

On the other hand, low temperature alteration is capable of modifying $\delta^{18}\text{O}$ to a great extent shifting them towards a higher value due to hydration, and weathering processes (Keller and Hoefs, 1995; O’Neil et al., 1969). The extent of modification by either seawater (Demény et al., 1998) or meteoric water (Doroshkevich et al., 2008) alteration will largely depend on the temperature during the interaction of fluids. For example, seawater introduced into a system with a temperature of about

300 °C will decrease $\delta^{18}\text{O}$ value by about 1–2‰ (Hoefs, 2009). Meteoric water with $\delta^{18}\text{O}$ ranging from +10 to –40 (Hoefs, 2009), and in order to decrease $\delta^{18}\text{O}$ value in the altered system, the system has to reach temperatures below 200–250 °C (Deines, 1989). A positive shift of meteoric water is explained by Ray and Ramesh (2000) as a fractionation followed by two-component Rayleigh fractionation. Interaction with seawater might also produce higher $\delta^{13}\text{C}$ values in carbonatites (Demény et al., 1998). Similarly, Keller and Hoefs (1995) assume that the Oldoinyo Lengai natrocarbonatites with $\delta^{18}\text{O}$ values <25 ‰ were completely exchanged their oxygen with meteoric water. The organic matter incorporated in the source or in the erupting magma is discussed above.

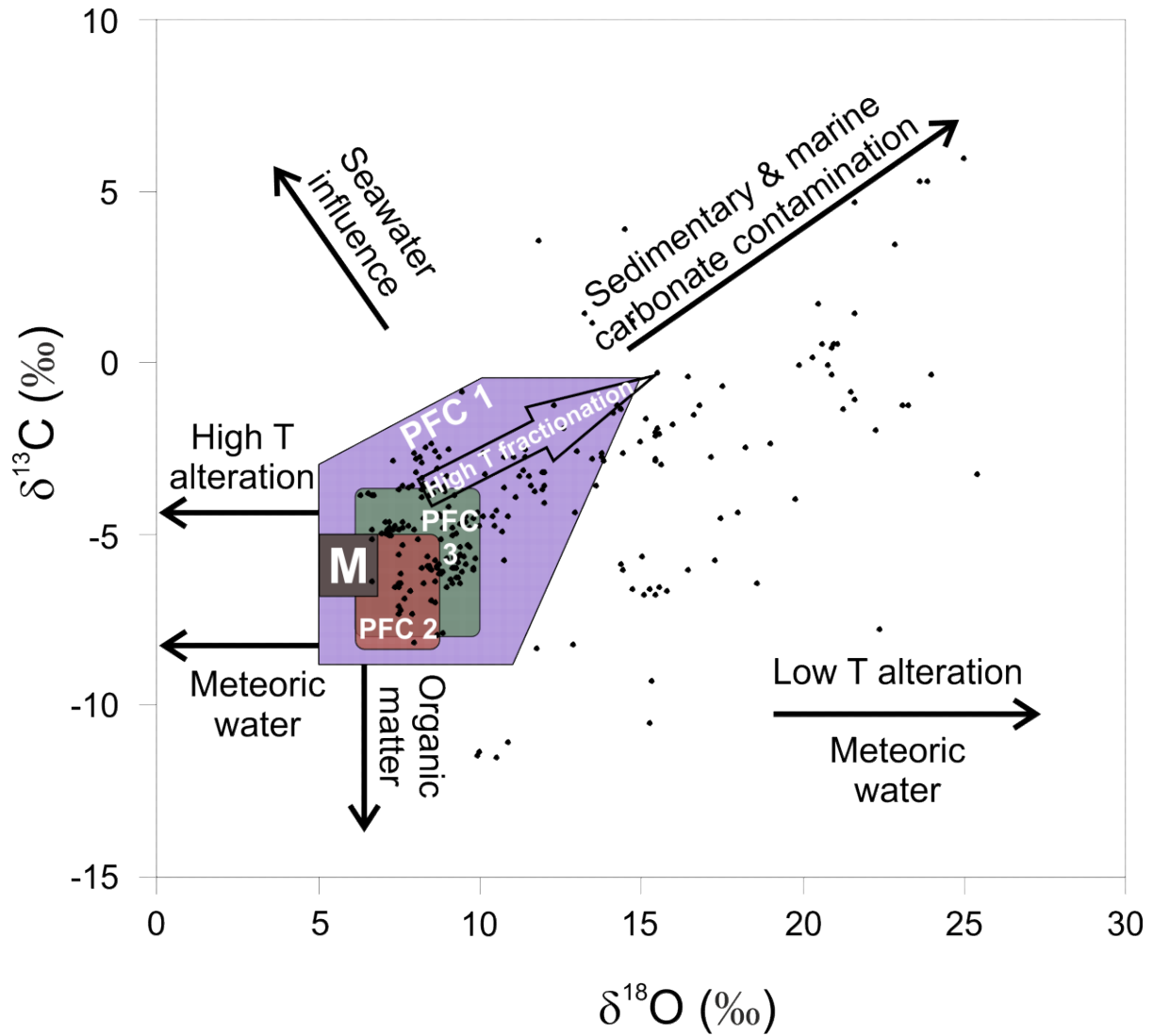


Fig. 1.8. Carbon and oxygen isotopic compositions (‰ relative to V-PDB and V-SMOW, respectively) of global carbonatites with fields related to different suits and directions of alteration and fractionation (Demény et al., 1998) of C–O isotopes. Data was compiled from the GEOROC database (Digis, 2024; Sarbas and Nohl, 2008). Mantle composition was redrawn from Ray and Ramesh (2006) compiled data of Cartigny et al. (1998), Deines, (1992), and Kyser, (1990). M – mantle, PFC 1 – primary carbonatite field by Ray and Ramesh (2006), PFC 2 – primary carbonatite field by Taylor et al. (1967), PFC 3 – primary carbonatite field by Keller and Hoefs (1995).

Sulfur consists of four stable isotopes with ^{32}S and ^{34}S representing more than 95% of total sulfur on Earth. For relative variation between sample and reference material, the $\delta^{34}\text{S}$ expressing variation in $^{34}\text{S}/^{32}\text{S}$ with respect to a standard reference material V-CDT (Vienna Canyon Diablo Troilite) is calculated as:

$$\delta^{34}\text{S} (\text{‰}) = \left[\left(\frac{^{34}\text{S}/^{32}\text{S}_{\text{sample}}}{^{34}\text{S}/^{32}\text{S}_{\text{V-CDT}}} \right) - 1 \right] \times 1,000 \quad (5)$$

Sulfur stable isotopes can be used in carbonatite isotope geochemistry since sulfur species presented in carbonatites are in the form of either sulfide (S^{2-}) or sulfate (SO_4^{2-}) with a high degree of $^{34}\text{S}/^{32}\text{S}$ fractionation depending on redox conditions of the melt. In oxidizing conditions (high oxygen fugacity) the sulfur is stable as sulfate, being commonly present in more evolved carbonatites resulting in the precipitation of barite or celestite. Minerals such as pyrite, chalcopyrite, or pyrrhotite are formed in reducing conditions (low oxygen fugacity; e.g., Wallace and Carmichael, 1992 and references therein). More about the impact of sulfur species on element mobilization is in Chapter 4. The magma evolution and related sulfur phase are critical for understanding REE precipitation and mineralization in REE-bearing hydrous systems (Weng et al., 2023). Indeed, the redox state influences resulting $\delta^{34}\text{S}$ values in carbonatite-hosted sulfides and sulfates identify the evolution sequence that helps to understand the degassing process of carbonatites from Catalão and Tapira complexes, Brazil (Gomide et al., 2013).

1.5.2. Insights from non-traditional stable isotopic data

Non-traditional stable isotopes (e.g., Ca, Mg, Fe, B, Cl) have gained growing attention in carbonatite research since they can offer unique views on the carbonatite petrogenesis and evolution. Here, I summarize some observations gathered so far for the elements that are essential for carbonatitic magmas (Ca, Mg, Fe) as well as boron due to its ability to trace recycled crustal material.

Apart from a large number of nuclides with very short half-life, calcium has nine known isotopes of which six are stable (^{40}Ca , ^{42}Ca , ^{43}Ca , ^{44}Ca , ^{46}Ca , and ^{48}Ca). For geochemical interpretations, Ca isotope compositions are typically reported as $\delta^{44/40}\text{Ca}$ expressing the deviation between a sample and standard (NIST SRM 915a, National Institute of Standard and Technology Material 915a; Eisenhauer et al., 2004) $^{44}\text{Ca}/^{40}\text{Ca}$ ratios in per mil:

$$\delta^{44/40}\text{Ca} (\text{‰}) = \left[\left(\frac{{}^{44}\text{Ca}/{}^{40}\text{Ca}_{\text{sample}}}{{}^{44}\text{Ca}/{}^{40}\text{Ca}_{\text{reference standard}}} \right) - 1 \right] \times 1,000 \quad (6)$$

Additionally, Ca isotopic data are sometimes reported as $\delta^{44/42}$ to avoid possible interference with ${}^{40}\text{K}$ and to account for mass-dependent fractionation effects.

Calcium isotope systematics is a powerful tool for marine geochemistry providing insights into the ocean compositions in the past through the studies of marine sediments, shells, and fossils (e.g., Zhu and Macdougall, 1998), but also serves as an efficient magma source tracker and differentiation not only on Earth, but also in extra-terrestrial bodies like on Mars (e.g., Magna et al., 2015). Since calcium is the principal component of the carbonatites, its isotopic composition has been used more frequently in recent years to determine for example the petrogenesis of different carbonatite types (Sun et al., 2021). Similarly, it is useful to clarify a period of massive carbonate production in the past in order to quantify the extent of outgassed CO_2 in the Eoarchean ($\sim 4\text{--}3.6$ Ga) ocean (Antonelli et al., 2021) indicating that the beginning of the plate tectonic process started prior to 3.5 Ga (e.g., Brown et al., 2020). Also, a fractional crystallization of carbonatites from the Aillik Bay, Eastern Canada, was excluded as a possible formation mechanism using calcium isotopes (Chen et al., 2024). The authors show a clear relationship between the wehrlite source and carbonatites supporting the theory that interaction between peridotite and rising carbonatite melt during ascend can result in the formation of a wehrlitic lithologies (described in 1.2.1). Calcium isotopes also helps to clarify changes in mantle geodynamics since by the end of Paleozoic, presence of recycled crustal carbonates in the source is more apparent in carbonatites younger than 300 Ma (Banerjee et al., 2021).

The changes in mantle geodynamics is also apparent in boron isotope systematics in carbonatites younger than 300 Ma. Boron isotopes consist of two naturally occurring stable isotopes ${}^{11}\text{B}$ and ${}^{10}\text{B}$. The $\delta^{11}\text{B}$ notation expressing the difference between ${}^{11}\text{B}/{}^{10}\text{B}$ and a reference standard material (NIST SRM 951, boric acid) is calculated as follows:

$$\delta^{11}\text{B} (\text{‰}) = \left[\left(\frac{{}^{11}\text{B}/{}^{10}\text{B}_{\text{sample}}}{{}^{11}\text{B}/{}^{10}\text{B}_{\text{reference standard}}} \right) - 1 \right] \times 1,000 \quad (7)$$

The variation of boron in nature can provide insights into a wide range of geochemical and environmental processes such as the presence of recycled crustal material in the mantle delivered via subduction. For example, it has been recognized that a significant difference exists between young

carbonatites that tend to have $\delta^{11}\text{B}$ values around 0 or > 0 in comparison to older carbonatites that exclusively yield largely negative $\delta^{11}\text{B}$ values (up to -8 ; Hulett et al., 2016) that can be perhaps related to the admixture of crustal material in the source. Additionally, boron isotopes were also used in addressing an extent of hydrothermal alteration linked with REE enrichment or depletion in the Miaoya carbonatite complex, China (Çimen et al., 2019).

Magnesium is second to oxygen in abundance among the rock-forming elements and it consists of 3 stable (^{24}Mg , ^{25}Mg , and ^{26}Mg) and 16 unstable isotopes (Young and Galy, 2004). For geochemical purposes, Mg isotopic data are reported as $\delta^{26}\text{Mg}$ values expressing variation in $^{26}\text{Mg}/^{24}\text{Mg}$ values with respect to reference material DSM-3 (Dead Sea Magnesium; Li et al., 2016; Young and Galy, 2004):

$$\delta^{26}\text{Mg} (\text{‰}) = \left[\left(\frac{^{26}\text{Mg}/^{24}\text{Mg}_{\text{sample}}}{^{26}\text{Mg}/^{24}\text{Mg}_{\text{reference standard}}} \right) - 1 \right] \times 1,000 \quad (8)$$

Magnesium has been considered a promising element to study magma differentiation since it has been found that during magma evolution, heavier Mg isotopes are fractionated from the lighter ones. This can be observed in isotope variation in Oldoinyo Lengai, Tanzania, where highly evolved silicate rocks presumably generated by silicate-carbonatite liquid immiscibility yield heavier $\delta^{26}\text{Mg}$ signatures ($\sim +0.03\text{‰}$) when compared to peralkaline silicate rocks that are not related to liquid immiscibility ($\sim -0.15\text{‰}$). In fact, the isotopic shift is most noticeable in natrocarbonatites where $\delta^{26}\text{Mg}$ reach up to $+0.37\text{‰}$ suggesting even more extent of differentiation for parental melts (Li et al., 2016). This result is in accord with the assumption of Berndt and Klemme (2022) and Hamilton et al. (1979) described in Chapter 1.2.2 and Fig. 1.5 that this phenomenon can be also related to fractional crystallization of carbonatite melts, enriched in heavy Mg, from residual melts (Li et al., 2016). Even more importantly, magnesium isotopes might also provide evidence of recycled carbon delivered to the mantle through the subduction zones detected in calciocarbonatites and magnesiocarbonatites (e.g., Wadi Tarr carbonatite or Tarim Province; Amsellem et al., 2023; Cheng et al., 2017, respectively).

Finally, the iron consists of four stable isotopes, namely ^{54}Fe , ^{56}Fe , ^{57}Fe , and ^{58}Fe . In stable isotope research, the $\delta^{56}\text{Fe}$ values expressing the variation in $^{56}\text{Fe}/^{54}\text{Fe}$ are calculated as follows using IRMM-014 standard as reference (provided by the Institute for Reference Materials and Measurements):

$$\delta^{56}\text{Fe} (\text{‰}) = \left[\left(\frac{{}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{sample}}}{{}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{reference standard}}} \right) - 1 \right] \times 1,000 \quad (9)$$

The reported $\delta^{56}\text{Fe}$ values so far carbonatites are extremely scarce (He et al., 2015; Zhang et al., 2021) in spite of their potential to unravel redox states of the carbonatitic magmas and the role of Fe-(oxy)hydroxides during silicate/carbonatitic melt fractionation and late-stage alteration processes characteristic for ferrocarbonatites. Zhang et al. (2021) recognized two sources of Fe in Mianning-Dechang REE belt carbonatites, China, based on coupled Fe and S isotopes. They suggested that the source of heavier Fe is sedimentary material whereas lighter Fe is predominantly derived from carbonatite magma.

1.6. Radiogenic isotope compositions

1.6.1. Behavior of parent/daughter elements during melting & magma differentiation

Since it has been inferred that large amounts of carbonatites represent products of liquid immiscibility from parental silicate melts, the behavior of parent/daughter elements that control their isotopic systematics is essential. In order to figure out the behavior of parent/daughter elements during the formation of carbonatitic melt and/or formation and differentiation of possibly carbonate-rich silicate melts, distribution coefficients (K_d) for carbonatitic melts and their counterparts for all possible carbonatite origins described in Chapter 1.2 need to be evaluated. The K_d data, mostly based on experimental works and sorted from the lowest recorded (K_d low) to the highest (K_d high) are collected from a global database Geochemical Earth Reference Model (GERM, 2024).

Carbonatites formed by **(I)** direct partial melting of peridotite suite that consists mainly of olivine, orthopyroxene, and clinopyroxene (Baker et al., 1995) will concentrate the majority of elements used in traditional radiogenic isotope analysis (Rb, Sr, Sm, Nd, U, Pb, Lu, Hf; note that K_d for HSE and Re–Os are described in Chapter 1.6.5.) as their K_d (peridotite/carbonatite) is as low as <0.16 (Brenan and Bruce Watson, 1991; Klemme et al., 1995). Therefore, these elements will strongly prefer to enter carbonatite melt in comparison to the residual peridotite keeping in mind that K_d is increasing in the case of Sm and Nd (~ 0.4) and Pb (~ 1.6). Yet, in the case of Pb, the determined high K_d of ~ 1.6 was performed at a rather lower temperature (1,200 °C), but very high pressure (5.5 GPa; Walker et al., 1992) whereas the determined K_d of 0.0055 for Pb was accessed by Blundy and Dalton (2000) using temperature of 1640 °C and pressure of 3.6 GPa.

During **(II)** fractional crystallization of silica-undersaturated silicate melts like nephelinitic, phonolitic, lamproitic, or kimberlitic (e.g., Lee and Wyllie, 1994; Nadeau et al., 2016; Weidendorfer et

al., 2016), K_d (mineral/silica-undersaturated melt) for orthopyroxene, clinopyroxene, leucite, nepheline, olivine, phlogopite, amphibole, biotite, and garnet are available. Not surprisingly, the highest distribution coefficients are observed for biotite that is capable of accumulating Rb ($K_d > 5$; Foley et al., 1996) whereas phlogopite yields K_d value for Rb of 1.44 (Schmidt et al., 1999). On the other hand, Sr is strongly incompatible and will remain in the residual melt as the highest measured K_d is 0.43 (amphibole in basanite; Adam and Green, 1994). This is in agreement with typically very low Rb/Sr ratios in carbonatite (0.014; Sarbas and Nohl, 2008). Garnet is only one mineral that has some potential to replenish the residual silicate magma in HREE such as Lu which yields a K_d value of 8 (Adam and Green, 2006). Other minerals are not capable of removing and fractionating parent/daughter elements from the residual melt during fractional crystallization suggesting that the melt would collectively become richer in Sr, REE, Pb, and HFSE during the progressive evolution of silicate to carbonatitic melt (Foley and Jenner, 2004; LaTourrette et al., 1995; Philpotts and Schnetzler, 1970; Schnetzler and Philpotts, 1970). Yet, some accessory minerals with high K_d cannot be omitted as if e.g., baddeleyite is formed and removed from the melt, the majority of Lu, Hf, and U will be sequestered (Klemme and Meyer, 2003), whereas apatite would extract Nd, Lu, and Sr ($K_d > 2$ and more; Dawson and Hinton, 2003; Klemme and Dalpé, 2003).

The K_d data between carbonatite melt and silicate melt are rather rare compared to solid-melt interaction and therefore, the behavior of parent/daughter elements during liquid immiscibility (**III**) partially relies on carbonatitic melt inclusions in the silicate minerals of alkaline rocks. For example, Guzmics et al. (2015) described carbonatite melt inclusions trapped in nepheline-hosted silicates showing preferential enrichment of all parent/daughter elements except Hf which is largely partitioned into silicates. The authors also stated that U^{4+} will prefer silicate melt whereas U^{+6} will partition into carbonatite melt indicating that redox conditions add another complexity to the system. On the other hand, carbonatite inclusions from the Dunkeldyk alkaline igneous complex, Tajikistan (Solovova and Girnis, 2012) indicate the partitioning of all above mentioned parent/daughter elements into silicates. This would be in agreement with the experimental work of Veksler et al. (2012) comparing natrocarbonatite and nephelinite melt (similar to Oldoinyo Lengai setup) showing that except Sr, the $K_d^{\text{carbonate/silicate}}$ were exclusively below 1, usually between 0.1 and 0.5. This dichotomy can be possibly explained by different PT conditions of experiments and different experimental melt compositions, especially the addition of volatile components such as F, Cl, and H_2O to the system can cause large differences in element behavior. At the same time, fluoride-silicate and phosphate-silicate ($K_d > 1 - 100$; Chakhmouradian and Zaitsev, 2012) partitioning might be also essential.

1.6.2. Rb–Sr and Sm–Nd isotope systematics: deciphering sources and evolution of carbonatitic magmas

One of the most important and powerful tools for the study of carbonatitic magmas is the coupled Sr–Nd isotopic systematics that can efficiently track down not only magmatic processes (melting, fractional crystallization, crustal contamination) but also late-stage alteration phenomena. Rubidium has two naturally occurring isotopes, ^{85}Rb (72.2%) and ^{87}Rb (27.8 %) whereas strontium has four isotopes, ^{84}Sr , ^{86}Sr (9.86 %), ^{87}Sr (7.0 %), and ^{88}Sr (82.6%) and ^{87}Rb decays by β^- decay with half-life about 4.96×10^{10} years (Kossert, 2003; Villa et al., 2015). Consequently, the amount of daughter ^{87}Sr is normalized to stable ^{86}Sr and expressed as $^{87}\text{Sr}/^{86}\text{Sr}$ for geochemical purposes. In comparison, samarium has seven naturally occurring isotopes ^{144}Sm (3.08%), ^{147}Sm (15.0 %), ^{148}Sm (11.3%) ^{149}Sm (13.8%), ^{150}Sm (7.37%), ^{152}Sm (26.7 %), and ^{154}Sm (22.7%); likewise, neodymium seven isotopes, ^{142}Nd (27.2%), ^{143}Nd (12.18%), ^{144}Nd (23.8 %), ^{145}Nd (8.3%), ^{146}Nd (17.2%), ^{148}Nd (5.8%), and ^{150}Nd (5.6%). The Nd isotopic systematics is based on the radioactive decay of ^{147}Sm with a half-life about 1.06×10^{11} (Villa et al., 2020) by α decay. Whilst daughter ^{143}Nd is normalized to radioactive ^{144}Nd (Jacobsen and Wasserburg, 1980) which is considered to be stable due to its very high half-life ($t_{1/2} = 2.29 \times 10^{15}$ years). For better visualization, a difference between $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ in the sample with respect to uniform (UR) and chondritic uniform (CHUR) reservoirs, respectively, is expressed through the ϵ notations as follows:

$$\epsilon_{\text{Nd}(t)} = \left[\left(\frac{^{143}\text{Nd}/^{144}\text{Nd}_{\text{sample}(t)}}{^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}(t)}} \right) - 1 \right] \times 10,000 \quad (10)$$

$$\epsilon_{\text{Sr}(t)} = \left[\left(\frac{^{87}\text{Sr}/^{86}\text{Sr}_{\text{sample}(t)}}{^{87}\text{Sr}/^{86}\text{Sr}_{\text{UR}(t)}} \right) - 1 \right] \times 10,000 \quad (11)$$

In general, a higher ϵ value reflects a higher concentration of radiogenic (daughter) isotope which in turn, means a higher parent/daughter elemental ratios (Rb/Sr and Sm/Nd) in the source and/or long-time isolated evolution required for a radiogenic composition (DePaolo, 2012; Faure, 1987; White, 2020).

Carbonatites are typically characterized by very high Sr contents (1,000 – 10,000 ppm) due to the generally high Sr (and other elements with similar behavior such as Ba) contents in the principal mineral phase – carbonate. On the other hand, the contents of Rb in carbonatites are much lower,

typically less than 50 ppm, with the majority of Rb being incorporated into mica (phlogopite, biotite) or monazite, both representing rather minor or even accessory phases. Consequently, a predominant amount of “pristine” carbonatites should exhibit very low Rb/Sr ratios and therefore, low $^{87}\text{Sr}/^{86}\text{Sr}$, unless some addition of material with higher Rb/Sr has been considered. Yet, the story with Sm–Nd isotopic system is much more complicated since carbonatites yield largely variable REE contents and Sm/Nd with respect to the nature of their source, mantle metasomatism, possible addition of recycled crustal component as summarized below and discussed in detail in Chapter 2, but also late-stage modification by percolation of REE-rich fluids.

Our statistical analyses of data from the global GEOROC database in terms of Sr–Nd composition of carbonatites illustrated in the $\epsilon_{\text{Sr}}-\epsilon_{\text{Nd}}$ plot (Fig. 1.4., 1.7., Fig. 2.2.) indicate that global carbonatites may be divided into three principal groups (**Group 1–3**) based on their Sr–Nd vector patterns while I note some overlap exists between individual Groups and therefore, these **Groups** are rather arbitrary to illustrate most important phenomenon at carbonatite petrogenesis arising from their Sr–Nd isotopic systematics.

Apart from that, some mantle-derived carbonatites, such as those from Newania, India (Ray et al., 2013) and the Karoo area in Southern Africa (Zeigler, 1992) display significantly decoupled Sr–Nd signatures characterized by low ϵ_{Nd} at given mostly unradiogenic ϵ_{Sr} that can be perhaps explained by ancient LREE-rich carbonatitic metasomatism and time-integrated evolution of the source with very low Sm/Nd. On the other hand, carbonatites with opposed decoupled signatures (very high ϵ_{Sr} at mantle-like ϵ_{Nd} ; e.g., studied Lemitar Mts, Chapter 2) plotting into the second quadrant (top right) most likely reflect late-stage interaction/overprint by fluids with crustal-like radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ compositions.

The majority of carbonatites (~ 60 %) fall into **Group 1** and are displayed in the first quadrant of the $\epsilon_{\text{Sr}}-\epsilon_{\text{Nd}}$ diagram. Thus, their parental melts were derived from variable enriched mantle sources with relatively high and positive $\epsilon_{\text{Nd}}(\text{i})$ reaching up to +6.6 and low to negative $\epsilon_{\text{Sr}}(\text{i})$ ranging between –20 and +30 depending on the enrichment of the parental melt. In this respect, these carbonatites may be a result of a mixture of EM I/EM II and HIMU or FOZO reservoirs (e.g., Bell and Simonetti, 2010; Yaxley et al., 2022). The majority of carbonatites from **Group 1** display mantle-like $\delta^{13}\text{C}$ and $\delta^{18}\text{C}$ signatures (Fig. 2.3.).

The **Group 2** carbonatites exhibit large variation in $\epsilon_{\text{Sr}}(\text{i})$ starting at ~ +20 and ending at +70 paralleled by a moderate range of $\epsilon_{\text{Nd}}(\text{i})$ exhibits slightly negative values ranging from –10 to –1. Such compositions cannot be attributed to either mixing of any mantle reservoirs as **Group 2** samples fall beyond their conventional boundaries or parental melt contamination by common, silicate lithologies (see discussion in Chapter 2). Therefore, this group appears to be a result of the incorporation of carbon-rich crustal material into parental melts during some stage of its evolutionary path. Such a

process, accompanied by shifting of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values to ~ 0 and $\sim 20\text{‰}$ (e.g., Li et al., 2018), respectively, is a result of the incorporation of either sedimentary material transported to the mantle by down-going oceanic slab as suggested by many studies (e.g., Amsellem et al., 2020; Hoernle et al., 2002; Li et al., 2018; Song et al., 2017; Wang et al., 2021) or through the contamination of parental melts by carbonate material during magma ascent (Doroshkevich et al., 2018). While the excessive modification of Sr–Nd isotopic systematics of carbonatite melt through contamination is rather unlikely due to its rather low temperature and typically very high contents of Sr and Nd itself, it might be possible for parental silicate melts prior to liquid immiscibility (e.g., Chandra et al., 2017). Therefore, the addition of carbonate material through crustal recycling is a more plausible scenario since they typically have ϵ_{Sr} values up to +70 while keeping ϵ_{Nd} at largely negative values (~ -7). and it is also supported by $\delta^{11}\text{B}$ values reported by Hulett et al. (2016), stating that the majority of carbonatites younger than 300 Ma contain an enriched (probably crustal) component.

A steady decrease in $\epsilon_{\text{Nd}}(\text{i})$ reaching values as low as -18 and a wide variation of $\epsilon_{\text{Sr}}(\text{i})$ ranging from ~ -10 to $+90$ is typical for rather ambiently defined **Group 3** carbonatites. This group was not recognized before as a separate unit, but individual carbonatite sites belonging to this Group were already explained as a result of the melting of some not-yet constrained enriched mantle (e.g., Gomes et al., 2011). Interestingly, these carbonatites are mainly linked with Archean–Paleoproterozoic cratons and their collision zones: Paraná-Etendeka Large Igneous Province, Kaapvaal, Sao Francisco, North China Craton, and Tamil Nadu. They span emplacement ages from 76 to 2,000 Ma. As we discuss in detail in Chapter 2, the regression line calculated from the median of $^{143}\text{Nd}/^{144}\text{Nd}$ values for individual carbonatite sites presented in **Group 3** with respect to their ages (Fig. 2.6) is $r^2=0.94$ and intersects the CHUR evolution line at ~ 2.8 Ga. Previously, some studies suggested that carbonatites are capable of sampling ancient metasomatized regions due to their low levels of fractional melting. For example, Comin-Chiaramonti et al. 2014 and references therein assumed that carbonatites linked with Paraná Basin are sampling some “ancient mantle reservoirs” that perhaps might be related to subduction processes since associated pyroxenites display negative Nb–Ta anomaly typical for subduction settings (Beccaluva et al., 1991). Later, Mitchell (2005) and references therein also suggested that the source of some plutonic potassic complexes can be some enriched lithospheric mantle affected by ancient metasomatism. However, since carbonatites are rather rare rocks in the geological record, they might have limiting potential to evidence of the involvement of Archaic material, and therefore, more common rocks have to be studied. A study was done on sixteen samples of basalts and picrites originating from Greenland–Iceland plume and is assumed that the head and its tail were sampling different primordial resources. Similar results are documented by Tusch et al.(2021) for Pilbara Craton in Australia where plume brought a Hadean pre-late veneer material.

Therefore, as presented in Chapter 2, such an unradiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ signature seen in **Group 3** carbonatites must be related to some sources with very low Sm/Nd ratios such as mantle that have been anciently metasomatized by slab-derived melts or by recycled crustal material incorporated into the mantle during Archean, in similar manner as (Woodhead et al., 2019) suggested for kimberlitic magmas. To test this hypothesis, we used an average global TTG (tonalite – trondhjemite – granodiorite) and sanukitoids suites as possible proxies for Archean slab-derived melts in a two-stage model (Fig. 2.7). First, a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of slab melts for an age where the $^{143}\text{Nd}/^{144}\text{Nd}$ of **Group 3** carbonatites intersects the CHUR line was calculated using present-day Sm–Nd ratios. Afterward, mixing this 2.7 Ga slab melt with a depleted mantle (as a representative of the “mantle-like” **Group 1** carbonatites) indicates that 2–10 % of this slab melt would be needed to form **Group 3** without adding an excessive amount of SiO_2 . Therefore, we suggest that the **Group 3** carbonatites could sample an anciently metasomatized mantle source by a low degree of melting or could be formed by liquid immiscibility of parental melt (still a low degree of melt) that was derived through the same mantle source.

Apparently, at least five different carbonatite sites at different locations around the world with different emplacement ages follow the same pattern characteristic for **Group 3**. These sites include Tamil Nadu in South India (Pandit et al., 2002), Rio Apa and Amambay regions in northeastern Paraguay (Comin-Chiaramonti et al., 2014; Gomes et al., 2011), at least partly Taohuala Mountain in North China (Xue et al., 2018), Anitápolis and Lages in Brazil (Comin-Chiaramonti et al., 2002), and Qieganbulake in northwestern China (Ye et al., 2013). This makes it very unlikely that all these bodies with different spatial and temporal evolution can gather their Sr–Nd isotopic signature from the crustal contamination of the same material to explain their co-appearance along the same Sr–Nd vector. Moreover, in case of crustal contamination, a large amount of crustal material would be involved and that would also be linked to a significant addition of typical “crustal” elements such as Si or Al correlated with Sr–Nd isotopic systematics, which is not observed at all for the **Group 3** carbonatites.

The above **Groups** boundaries were set as an auxiliary border, they do not reflect strict borders, because groups are inter-mixed and the boundaries have thus to be used with caution.

1.6.3. Lead isotopic systematics of carbonatites

Lead consists of four naturally occurring isotopes ^{204}Pb (1.4 %, stable), ^{206}Pb (24.1 %), ^{207}Pb (22.1 %), and ^{208}Pb (52.4 %). This systematics utilize three different decay chains: ^{238}U with corresponding half-life 4.47×10^9 years to ^{206}Pb , ^{235}U (7.04×10^8 years) to ^{207}Pb , and ^{232}Th (1.4×10^{10} years) to ^{208}Pb . Thus, since only ^{204}Pb represents the stable isotope, lead isotopic data are expressed as ratios of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ and are widely used since the pioneering data for carbonatites

has been presented for some Archean carbonatites (Tilton, 1983) providing a piece of evidence for the presence of time-integrated depleted mantle as the source. Yet, I note that bulk-rock Pb isotopic systematics can be sometimes largely altered by late-stage processes that induce precipitation of U-Th-rich minerals (e.g., on Fen Complex). For this reason, some studies determined Pb/Pb ratios in calcite grains from carbonatites and carbonatite xenoliths to constrain mantle sources and possible mixing of different mantle reservoirs. For example, Xu et al. (2008a) suggested that the source of Shaxiongdong carbonatites, China, is represented by a mixture of HIMU and EM I reservoirs whereas the Oka carbonatite complex, Canada, is from the Pb–Pb perspective considered to reflect a mixture of HIMU–EMI–ADM (ancient depleted mantle component; $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7025$, $^{206}\text{Pb}/^{204}\text{Pb} \sim 18$; Chen and Simonetti, 2015). Similarly, Rukhlov et al. (2015) suggested a deep “undegassed” mantle source similar in composition to present-day FOZO with admixtures of HIMU, EM, and/or primordial material such as recycled Hadean crust that have been sampled by mantle plume originating in D” layer (the zone between the lowermost mantle and the Earth’s outer core). A Dupal anomaly, a distinct geochemical signature typical for mantle rocks in the southern hemisphere (Dupré and Allègre, 1983; Hart, 1984), is also apparent in $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios in carbonatites as reported in Brazilian carbonatites from Catalão region (Toyoda et al., 1994). A Dupal anomaly suggests an asymmetry in mantle Pb composition which may be caused by the addition of ancient crustal material or altered oceanic crust to some mantle parts (Regelous et al., 2009) or by deep-seated plumes that can bring primordial material from lower mantle/core-mantle boundary (Castillo, 1988) or it shows a heterogeneity of the mantle (Parai et al., 2012).

Lead isotopes can be also used as geochronological tracers. Despite the rarity of zircons in carbonatites because of their SiO₂-poor nature, zircon and baddeleyite from the Phalaborwa, South Africa collectively yield a direct age of 2059.8 ± 1.3 Ma (2σ ; Wu et al. (2011). Yet, the presence of zircon grains in carbonatites needs to be treated with caution, because carbonatite bodies often are infiltrated by a late-stage carbonatite melt generation that can cause alteration of zircon grains (Tichomirowa et al., 2013). The U–Pb geochronology of carbonatites can also be performed using other minerals as shown in Ghobadi et al. (2022), where the age of Kaiserstuhl carbonatites was determined on pyrochlore (15.35 ± 0.24 Ma) and perovskite (14.56 ± 0.86 Ma). Besides, developments in instrumental techniques now also allow determining U–Pb crystallization ages of apatite from carbonatites using LA-ICPMS, as exemplified for Amba Dongar (Fosu et al., 2019).

1.6.4. Lu-Hf isotopes: an interplay between carbonate and non-carbonate fractions

Another powerful isotopic tool in carbonatite research is represented by the Lu-Hf isotopic system commonly used to investigate Earth’s mantle differentiation and the nature of mantle sources. This system benefits from radioactive decay of ^{176}Lu (representing 2.6 % of total Lu) to ^{176}Hf with a long

half-life of approximately 3.7×10^{10} years whereas the second Lu isotope is stable (^{175}Lu ; 97.4%). In comparison, hafnium has five stable isotopes, namely ^{176}Hf (5.26 %), ^{177}Hf (18.6 %), ^{178}Hf (27.3 %), ^{179}Hf (13.6 %), ^{180}Hf (35.1 %), and one radiogenic with long half-life (^{174}Hf ; $\sim 7 \times 10^{16}$ years).

Similarly, to Nd isotopes, the Hf isotopic composition ($^{176}\text{Hf}/^{177}\text{Hf}$) difference between the sample and chondritic uniform reservoir is expressed by ε_{Hf} , which is calculated as follows:

$$\varepsilon_{\text{Hf}(t)} = \left[\left(\frac{^{176}\text{Hf}/^{177}\text{Hf}_{\text{sample}(t)}}{^{176}\text{Hf}/^{177}\text{Hf}_{\text{CHUR}(t)}} \right) - 1 \right] \times 10,000 \quad (12)$$

Rukhlov et al. (2015) studied Hf isotopic compositions of carbonatites spanning in age from 95 to 2691 Ma and obtained data shows a wide range of initial ε_{Hf} spanning from -12 to +32 with the younger carbonatites having a more broad range of initial ε_{Hf} , collectively indicating that the source of carbonatites can be either depleted or enriched mantle (Bizzarro et al., 2002). Yet, most radiogenic samples fall beyond all mantle reservoirs, notably depleted mantle, and therefore cannot be a result of simple mixing, which is also noticeable from the whole-rock analysis of Polák et al. (2020; Fig. 1.9). As stated above, during melt evolution, dissolution and re-precipitation of zircon happened and since zircon is a principal Hf carrier, this can potentially have some impact on Hf isotopic systematics. Indeed, during this event, high Lu/Hf ratios from the co-existing phases can be incorporated into zircons (Tichomirowa et al., 2013), and therefore, lead to the development of highly radiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ values even during a short period of time. Typically high Lu/Hf ratios of some possible long-live carbonatite source as carbonatites would develop extremely radiogenic Hf composition which has not been observed and therefore, such a scenario can be ruled out (Bizimis et al., 2003). Further, maximum Lu/Hf fractionation between the source and the carbonatite melt, during direct melting (liquid immiscibility was ruled out by disequilibrium of carbonate and non-carbonate phases, described lower), is determined by $D_{\text{Lu}}/D_{\text{Hf}}$ which is closer to one or greater than one unity suggesting that the carbonatite source would have a different Lu and Hf concentration than primitive or depleted mantle (Bizimis et al., 2003). From a wide variation in initial ε_{Hf} reported by Rukhlov et al. (2015), they assumed that the depleted mantle was formed by a major differentiation event before 3 Ga. This is supported by the fact that most of the non-carbonate fraction published in Schweitzer (2019) falls between DMM and CHUR for at least 3 Ga. In this respect, slightly negative ε_{Hf} can be the result of

the melting of the metasomatized enriched lithospheric mantle as described in the Phalaborwa complex (Wu et al., 2011).

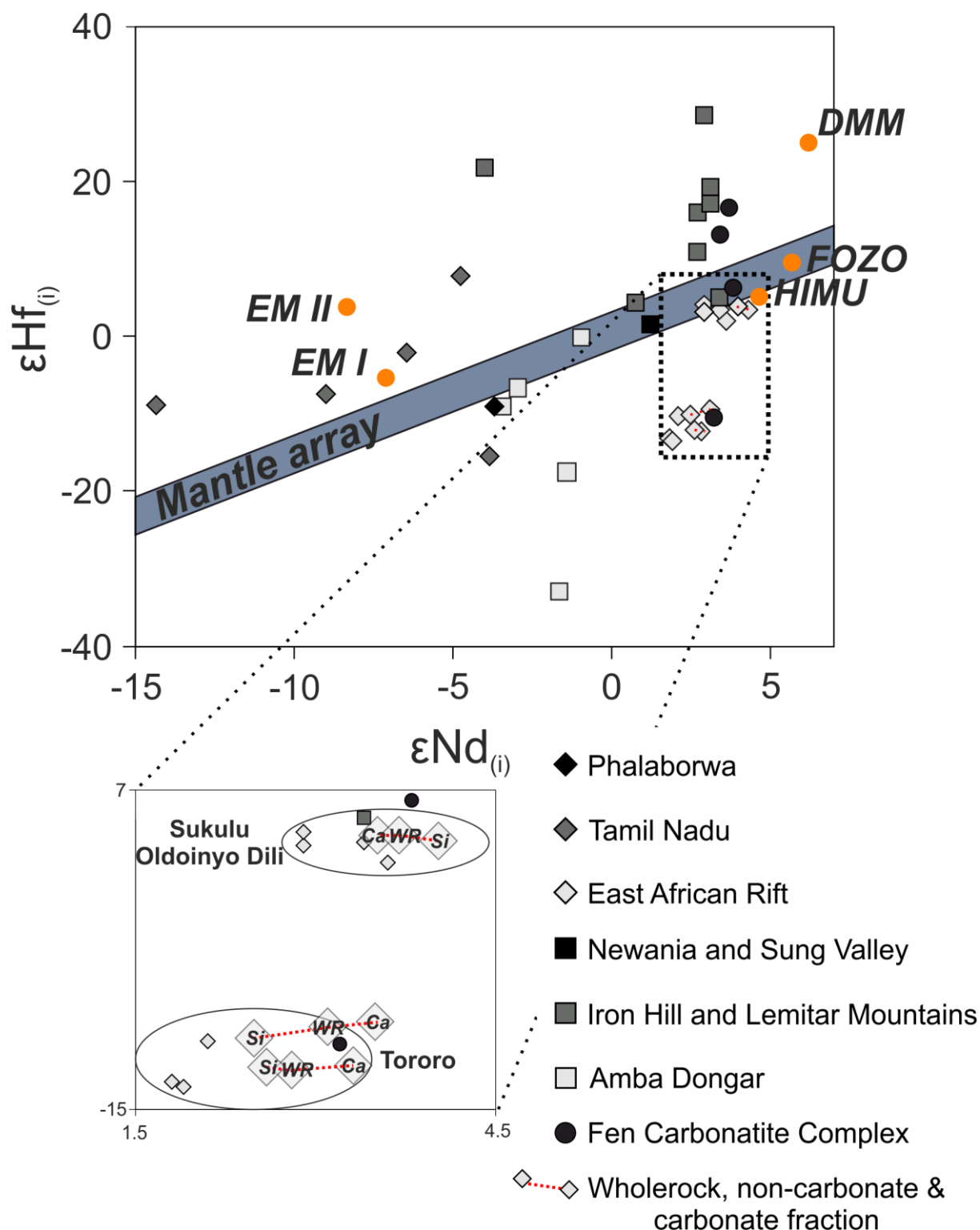


Fig. 1.9. Bulk-rock as well as mineral fraction Hf–Nd isotopic data expressed in $\epsilon_{\text{Hf}}(i)$ – $\epsilon_{\text{Nd}}(i)$ diagram (also unpublished data of the author is given), carbonate fraction estimated from measured non-carbonate fraction and whole-rock. Ca – carbonate fraction, Si – non-carbonate fraction, WR – whole-rock. Values of different mantle reservoirs taken from (Hofmann, 1997; Rukhlov et al., 2015; White, 2020; Zindler and Hart, 1986).

The study of trace element and/or isotopic composition of carbonate and non-carbonate fractions in carbonatites is essential since both fractions are characterized by very high and low Lu/Hf ratios, respectively, and therefore understanding an interplay between these two fractions might help to determine the magma source, its evolution, and melt as well as late-stage enrichments. Such study can be employed by various techniques, for example, mineral fractions separation (physical or chemical by heavy liquids or selective leaching) followed by chemical dissolution in case of physical separation and proper ion exchange chromatography, or *in-situ* laser ablation ICP-MS analyses of individual carbonate and non-carbonate mineral phases.

The chemical separation technique was used to determine Nd, Sr, and Hf isotopic composition of carbonate and non-carbonate phases (Bizimis et al., 2003) in young carbonatites from the East African Rift zone, Canadian Craton, and South African craton. The results suggest that the Sr and Nd isotopic system is dominated in the carbonate phase. On the other hand, the non-carbonate fraction holds the majority of Hf, Zr, and Ti. The isotopic disequilibrium between carbonate and non-carbonate phases was also found and explained by different sources in both fractions. However, during the replicate analyses performed by myself for young samples (Tororo and Sukulu; <40 Ma), such dispersion variation was either not observed (Fig. 1.9) or on a very limited number of samples, and therefore, this hypothesis needs to be evaluated by further experiments.

This can be perhaps related to different protocols that were used to obtain carbonate and non-carbonate fractions. For example, most studies typically do not split non-carbonate fraction into more detailed fractions and thus, an apatite being an important phase in terms of $^{176}\text{Hf}/^{177}\text{Hf}$ is often omitted despite its possible dissolution at more or less neutral pH (4-7, which corresponds to 0.0001–0.0000001 M HCl) proposed by several dissolution methods (Dorozhkin, 2012) and as stated above, the apatite are capable to carry a significant amount of Sr and other elements.

Possible Lu–Hf isotopic disequilibrium between carbonate and non-carbonate phases in Lu–Hf isotope systematics was discussed by Schweitzer (2019) recognized that calculated ages from both fractions of different carbonatite complexes are largely different from each other. For example, carbonate fractions from the Fen carbonatite complex always gather more negative ϵ_{Hf} values than non-carbonate fraction or a whole rock. The author attributes this phenomenon to overprinted carbonate fraction rather than isotopic disequilibrium based on carbonate and non-carbonate phases.

1.6.5. Highly siderophile elements and Re–Os isotopes: valuable tracers of mantle processes but not useful for carbonatites?

Highly siderophile elements (HSE) form the group of chemical elements with very high partitioning ($>10^4$) into the metal phase, or in the case of the absence of metal, to the base metal (Fe–Ni–Cu)

sulfides (Harvey and Day, 2016) in comparison to silicates. They comprise platinum group elements (PGE – Os, Ir, Ru, Pt, Rh, Pd) and Re with Au. Platinum group elements are divided into two groups based on their similar properties. Iridium-group (IPGE) containing Os, Ir, and Ru, and platinum-group (PPGE) consisting of Pd and Pt while Rh is standing as a transition metals sharing some properties of both groups. The HSE are characterized by high to very high melt temperatures, rather low volatility (except Os), and high resistance to weathering processes. Due to their siderophile character, HSE are typically found in very low concentrations in the Earth's crust (< 1 ppb; Day et al., 2016a), but their concentrations increase at the mantle (several ppb of each element) reaching maximum in the core (several orders of magnitude higher; McDonough and Sun, 1995) due to extreme affinity of HSE to Fe–Ni alloys. At the same time, due to different electronegativity and oxidation states, rhenium and gold do not act coherently with the rest of the elements. The PGE are either hosted by the metallic state or bond with chalcogens (S, Te, Se) or some pnictogens (As, Sb, Bi; Harvey and Day, 2016). Tredoux et al. (1995) suggested that the PGE are presented in the melt as metallic clusters that consist of 50–100 atoms, rather than cations. Those clusters are stabilized by ligands, namely S, As, Sb, or Te, not by classical chemical bonds, but rather by adsorption. However, such a process requires high temperatures starting at 1060 °C for Au and as high as 3000 °C for Os.

In addition to HSE elemental contents, unique insights into various geological processes are gathered through the Re–Os isotopic system. In comparison to other traditional radiogenic systems summarized above (e.g., Sm–Nd, Lu–Hf), both elements are hosted not in silicates but largely in sulfides/metals providing intriguing constraints on the mantle and melt evolution processes from different perspectives. Rhenium occurs in the form of two isotopes. ^{185}Re and ^{187}Re (62 %), with the latter decays to ^{187}Os with relatively half-time (4.23×10^{10} years). Osmium is represented by seven isotopes with mass ^{184}Os , ^{186}Os (1.58 %), ^{187}Os (1.6 %), ^{188}Os (13.3 %), ^{189}Os , ^{190}Os , ^{192}Os with radiogenic ^{186}Os being produced through the decay of radioactive ^{190}Pt .

The difference between osmium isotopic composition ($^{187}\text{Os}/^{188}\text{Os}$) in the sample and some ambient chondritic uniform reservoir is given by the γ_{Os} notation expressed as:

$$\gamma_{\text{Os}(t)} = \left[\left(\frac{^{187}\text{Os}/^{188}\text{Os}_{\text{sample}(t)}}{^{187}\text{Os}/^{188}\text{Os}_{\text{CHUR}(t)}} \right) - 1 \right] \times 100 \quad (13)$$

The absence of HSE partitioning coefficients data for carbonatite/silicate melt does not allow direct assessment with respect to the behavior of HSE during carbonatite liquid immiscibility. Yet, some insights can be predicted from K_d of sulfide/silicate and sulfide/carbonate partitioning. In this respect, $K_d^{\text{sulfide/silicate}}$ (Fleet et al., 1996; Mungall and Brenan, 2014) overlap or are slightly higher than $K_d^{\text{sulfide/carbonate}}$ (Chowdhury et al., 2021; Pearson et al., 2004) with sequence $\text{Re} < \text{Pt} < \text{Pd} < \text{Ru} < \text{Ir} <$

Os starting at K_d 10^3 for Re for both, silicate and carbonate and ending at value 10^5 for carbonate and 10^6 for silicate for Os. HSE are in general compatible during partial melting, retained in the mantle, and should be sampled by large degrees of melting (Pearson et al., 2004). However, the HSE solubility strongly depends on fS_2 , which is strongly dependent on the pressure, and fO_2 related to temperature (Mungall and Brenan, 2014). For the Re–Os isotope systematics, it is important to take into account the compatible character of Os which remains in the residue whereas Re is generally incompatible, thus entering the melt during partial melting. In fact, all IPGE are more compatible than PPGE (Fleet et al., 1996) which results in a positive slope of HSE in peridotites (e.g., Ackerman et al., 2013a).

In the case of mantle-derived melts, the predominant amount of studies have been focused on komatiites, picrites, arc lavas, and basaltic rocks that include MORB and/or OIB (e.g., Dale et al., 2012; Day, 2013; Day et al., 2016a,b; Ireland et al., 2009; Peters et al., 2016). Only in a small part, some data have been presented for CO₂-rich alkaline silicate rocks such as lamprophyre, lamproite, or Mg-rich komatiite (Gan and Huang, 2017; Krmíček et al., 2020; Maier et al., 2017; Tappe et al., 2020b) with, at least for Re–Os isotopic systematics, sometimes dubious results related to very low Os contents. In the case of carbonatites, highly siderophile element and Re–Os isotope research has been addressed by a very limited number of studies, and some of them only reported PGE contents (Fontana, 2006; Sazonov et al., 2021; Tappe et al., 2020b; Xu et al., 2008a). This is connected with two principal challenges. First, extremely low concentrations of HSE (units to hundreds of ppt) are characteristic for carbonatites. Second, the sample decomposition that is typically accomplished in sealed Carius Tubes (Shirey and Walker, 1995) during a high temperature (up to 260 °C) generates large CO₂-overpressure that is commonly associated with the explosion of the tubes. To overcome this problem, a so-called decarbonization is performed in several batches by variable diluted HCl before the sample decomposition has been invoked (Xu et al., 2008a). Following this pioneering study, we performed several tests using four different decarbonization protocols (in detail described in Chapter 3) using reference material COQ–1 (carbonatite, Oka complex, USGS) with Carius tubes containing a sample, reverse *aqua regia* and spikes remained cooled by the mixture of dry ice slush and ethanol to lower the vapor pressure. Inverse *aqua regia* (5:4 ratio of nitric to hydrochloric acid) is used to increase the oxidizing effect on Re as well as Os to create moderately volatile oxides (Shirey and Walker, 1995). After decomposition is done and Carius tubes are about to be opened, the tubes have to be cooled with the dry ice slush again to lower the internal pressure and prevent possible loss of volatile Os. Overall, the results confirmed that the selected method of decarbonization (HCl, HBr–HCl, etc.) induces no difference to obtained HSE contents and ¹⁸⁷Os/¹⁸⁸Os values, but experiments with different sample weights reveal another problem – a large-scale nugget effect observed in carbonatites. The nugget effect is amplified by the naturally low abundance of HSE in samples impoverished in sulfur such as carbonatites that have been even recrystallized during hydrothermal alteration. This can be best illustrated in the case of calciocarbonatite from the Fen

complex (CFN 3) where the first analyses yield an Os concentration of 1 ppt while the second yields an Os content of 8 ppt. If we omit Os blank (< 1 pg), such a low concentration yields a difference of 800% between two replicates even when up to ~ 4 g of weighted material was used (this was the highest documented nugget effect). A nugget effect can be caused by the largely heterogeneous presence of microinclusions scattered in the grinded sample powder, which would be hard to homogenize to more extent even by repeated quartation or similar. Such nugget effect can be well-explained by the fractionation of platinum-group elements (PGE) into clusters randomly deployed as described in the study done by Tredoux et al. (1995). A selective complexing of PGE into ligands was also proposed by some other researchers (e.g., Helmy and Bragagni, 2017). In any case, both explanations of the nugget effect are difficult to prove and spot due to the extremely low concentration of HSE and their characteristic random distribution in the geological materials.

So far, there are no information available on which phases in carbonatites are responsible for the hosting of the predominant budget of HSEs. Yet, we can infer by what is already known about the principles of siderophile element behavior and minerals that can be found in carbonatites, that they should be largely hosted by some sulfide phases. In this respect, base metal sulfides (BMS) are thought to be major controls of the PGE budget (e.g., Brenan et al., 2016; Luguet et al., 2001) with pyrrhotite being a major BMS in magmatic rocks (Rudashkevsky et al., 2004; Schweitzer, 2019). However, in carbonatite complexes, no correlation between individual/total HSE and sulfur has been found. Similarly, in our pilot study focused on carbonatites and associated silicate alkaline rocks from Tamil Nadu, India (Ackerman et al., 2019), sulfides are rare and if so, they are represented solely by pyrite (be aware of pyrites formed by secondary processes with unrealistically elevated Re concentrations) that is capable to host a wide range of Re, but rather very low PGE. Typically very low PPGE content in pyrite might be related to replacement (so-called pyritization) of parental BMS where IPGE can be accommodated through the exsolution from MSS (Mansur et al., 2021) or pyrite can also represent the primary, mantle phase (e.g., Cafagna and Jugo, 2016; Lorand, 1989). On the other hand, we concluded (Polák et al., in press) that extremely high Re contents detected in some carbonatites (e.g., Fen complex in Norway) can be rather explained by the addition of Re-rich molybdenite during late-stage alteration. Moreover, the concentration of PGE in individual BMS might also depend on the redox conditions (Aulbach et al., 2016) and oxidation state of the sulfur as S^{2-} will preferentially enter silicate melt whereas S^{6+} will partition into carbonatite melt (Guzmics et al., 2015). Nevertheless, low concentrations of HSE in carbonatites match well with a low concentration of sulfur. This is rather surprising as experimental works reveal that carbonatitic melts are capable of dissolving larger amounts of sulfur than in the case of basaltic melts (the sulfur amount is dependent on FeO content; Jorgenson, 2017) and therefore, hints that a significantly higher amount of HSE should be observed. This apparent dichotomy testifies for HSE-S removal during some stages of carbonate-rich melt evolution which is depicted in detail in Polák et al. (in press) representing

Chapter 4. Primary sulfur contents (solubility) in carbonatites can reach up to 0.9 wt.% in FeO free melt (Helz and Wyllie, 1979; Jorgenson, 2017) suggesting that during carbonatite liquid immiscibility, S as well as HSE should be theoretically concentrated in the carbonatite melt to some extent. Yet, since the recent study of Polák et al. (in press) highlights generally very low HSE contents irrespective of age, carbonatite type, etc., some other process must interplay (e.g., the role of fluid phase, atomic clustering). In fact, clustering might also explain a negative slope that can be seen in calciocarbonatites between Os-Ir and most likely Ru as well (described in the next paragraph).

A pioneering study by Ackerman et al. (2019) on carbonatites from Tamil Nadu, India reveals for this time, characteristic negative slope in IPGE when normalized to some primitive mantle values (e.g., Becker et al., 2006) with Os_N/Ir_N being reported in a wide range between 2.3 to 15. This phenomenon was attributed to the selective dissolution of principal IPGE carriers, like alloys or high-temperature sulfides, during the percolation of e.g., sulfur-undersaturated melts in the upper mantle. This normalized range was later extended by Polák et al. (in press) on more carbonatite samples at global scale to 1.5–15, also determined negative Os_N/Ir_N (Ru_N) exclusively for calciocarbonatites and Si-rich calciocarbonatites while at the same time, no correlation between the content of HSE and CaO contents or between individual HSEs were found in agreement with the results of Schweitzer (2019). Apparently, a similar mode of HSE fractionation was previously described in three other sites, but for the basaltic rocks. First, for flood basalts from Guizhou Province in China where IPGE depletion is assumed to be a result of laurite (RuS_2) and Os-Ir-Ru alloys both formed and being enclosed in early crystallizing phases like chromite and olivine subsequently removed from the melt (Qi and Zhou, 2008). Second, such signatures (but partly with positive anomaly in Ru) were reported for some Deccan and Réunion basalts and xenoliths from Gujarat and Maharashtra States in India where Peters et al. (2017, 2016) assumed that examined lavas preserve HSE fractionation patterns from parental magma and inherited signature. Lastly, Zhenyuan lamprophyres from China yield large IPGE fractionation mode. Here, according to Gan and Huang (2017), low PGE contents reflect early S-saturation of the parental melt followed by sulfide removal and therefore early crystallization of mafic minerals (IPGE are considered to be compatible at phases that are removed during the initial stages of mafic magma fractionation) together with laurite and Os-Ir-Ru alloys leading to the depletion of fractionated melt in the IPGE. In contrast, our results summarized in Polák et al. (in press) and given in Chapter 4 suggest that the overall low content of HSE in carbonatites as well as the limited presence of HSE-bearing carriers is caused by the separation of sulfide or S-rich silicate melts during liquid immiscibility. As shown in Chowdhury et al. (2021) the $D^{sulfide/carbonate}$ is higher for Os over a Ru and due to the high distribution coefficients, are IPGE sequestered into S-rich melts and thus, later formed calciocarbonatites are characterized by Os-Ir-Ru depletion. Moreover, modeled CO_2 -rich magmas are characterized by $Os_N/Ru_N < 1$ unless the source is unrealistically depleted in S.

Possible crustal contamination of parental carbonatitic magmas that can potentially result in radiogenic isotopic modifications has been debated (see above) since such a process is difficult to recognize through the common Rb-Sr and Sm-Nd isotopic systems since the daughter elements are typically present in high concentrations in carbonatites. On the other hand, due to the low concentration of HSE and radiogenic $^{187}\text{Os}/^{188}\text{Os}$ nature of continental crust in opposition to mantle-derived melts, Re-Os can serve as a powerful tracer of contamination keeping in mind also other processes that can lead to any disturbance of Re-Os systematics (HSE mobilization, the contribution from hydrothermal alteration, etc.). Notably, detected ratios of $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os(i)}$ in carbonatites are extremely high in most cases and therefore, unrealistic with respect to the nature of possible mantle sources and/or crustal contaminants. In the case of $^{187}\text{Re}/^{188}\text{Os}$, the values span from 0.096 to 25,000 while the chondrite value is about 0.4019 (Shirey and Walker, 1998), and a value of 0.428 has been estimated for primitive upper mantle (PUM; Meisel et al., 1996). For $^{187}\text{Os}/^{188}\text{Os}$, the chondritic ratio is 0.127 (Shirey and Walker, 1998) and for PUM 0.129 (Meisel et al., 1996), while the global carbonatite dataset accessed by our studies (Ackerman et al., 2019; Polák et al., in press) yield initial $^{187}\text{Os}/^{188}\text{Os}$ values ranging from largely negative to +16.5 that stands for γOs value of $\sim 13,000$. Highly positive γOs value is closely linked with crustal contamination as an average continental crust has a $^{187}\text{Re}/^{188}\text{Os}$ ratio of around 50 (Shirey and Walker, 1998 and references therein), so only a small portion of global carbonatites can potentially undergo contamination by crustal material to variable extent. This is in agreement with the highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios found in samples from Kovdor (ratio ~ 2.1 ; Schweitzer, 2019), but Lee et al. (2006) did not assume any crustal contamination at the Kovdor site. Yet, one of the possible crustal contaminants can be either eclogite and/or granulite, because both lithologies can contain variable amounts of sulfides with extremely radiogenic signatures developed over time (Aulbach et al., 2016, 2010). High ratios of $^{187}\text{Os}/^{188}\text{Os}$ near 3.7 can be also found on the subduction zone in Java (Alves et al., 1999) that can be attributed to the supposed radiogenic $^{187}\text{Os}/^{188}\text{Os}$ nature of subduction-related fluids (e.g., Brandon et al., 1996). In this respect, it has been suggested that Os mobility in the slab-derived fluids strongly depends on oxygen fugacity and chlorine contents and that the Re influx into the sub-arc mantle also occurs (Gan and Huang, 2017 and references therein). However, if an increased ratio of $^{187}\text{Os}/^{188}\text{Os}$ would be a result of the addition of Re into the source, a positive correlation between $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ should be presented, which is not the case for the sole (Ackerman et al., 2019) and/or global carbonatite (Polák et al., in press) suites.

Gan and Huang (2017) explained high $^{187}\text{Os}/^{188}\text{Os}$ ratios in lamprophyres by long-lived metasomatic mantle reservoir with high Re/Os ratio. Such time-integrated source with an evolved radiogenic signature can be potentially sampled by S-undersaturated carbonated magmas however, the signature should be rather constant at least at individual carbonatite localities with rather a small fluctuation which is not observed (Polák et al., in press). Another possibility can be connected with the

known volatility of rhenium during degassing (e.g., Yudovskaya et al., 2008) leading to its partitioning into a volatile phase that will later metasomatized some mantle lithologies being subsequently melted to produce carbonatitic magmas. Finally, high $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ values are characteristic of organic-rich crustal lithologies such as black shales which are attributed to the organophilic nature of both Re and Os (Rooney et al., 2024 and references therein). Thus, black shales can accumulate a significant amount of Re and Os, the former being present in larger quantities leading to highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ being developed over time. However, selective contamination of carbonatitic magmas by black shale lithologies can be ruled due to largely variable carbon isotope signatures ($\delta^{13}\text{C}$) being reported for carbonatites (-1.95 to -5.95 ‰) while black shales reaching commonly $\delta^{13}\text{C}$ values of up to -30 ‰ (Jenkyns and Clayron, 1986).

Chapter 2

A long-lived enriched mantle reservoir evidenced by neodymium isotope systematics of carbonatites

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Abstract

The longevity of carbonatites in the geologic record since ~3 billion years ago (Ga) allows us to track the evolution of carbon-bearing mantle sources throughout the Earth's history. Recent investigations also indicate that many carbonatite sources contain a significant proportion of recycled sedimentary material. Yet, such a mechanism cannot explain particularly unradiogenic initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios observed in many carbonatites worldwide with emplacement ages ranging from ~2.0 Ga to 76 Ma due to inconsistency of Sr isotope compositions in recycled sedimentary materials which are too radiogenic compared to $^{87}\text{Sr}/^{86}\text{Sr}$ in these low- $^{143}\text{Nd}/^{144}\text{Nd}$ carbonatites. Here, we argue that such unradiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ compositions with $\epsilon_{\text{Nd}}(\text{i})$ values as low as -18.3 can be best explained by a significant input of low-Sm/Nd (<0.17) slab-derived melts that must have been incorporated into the mantle source parental to these low- $^{143}\text{Nd}/^{144}\text{Nd}$ carbonatites at least 2.5 billion years ago and perhaps even earlier. A close spatial and temporal relationship between the events of carbonatite extrusions and the life cycles of super-continentals also indicates that the emplacement of carbonatite magmas is closely linked to major phases of the formation and breakup of super-continentals since the Meso/Neoproterozoic.

Keywords: Carbonatites, long-lived enriched mantle, super-continentals

2.1. Introduction

Carbonatites span the emplacement ages from the Archean (~3.0 Ga) to present and are found on all continents (see Woolley and Kjarsgaard, 2008a), including the sole known occurrence in Antarctica (Hall et al., 1995). Their specific mineralogy (>50 modal % igneous carbonate phases), and often extreme enrichments in elements such as light rare earth elements (LREE), Nb, Ta, Th, and U make them an attractive research target for igneous petrogenesis, mantle geochemistry, and economic geology (Jones et al., 2013; Krishnamurthy et al., 2000; Xu et al., 2010; Yang et al., 2011; Yaxley et al., 2022). Carbonatites are associated with a wide range of geotectonic settings which include intra-continental extensional regimes (e.g. the East African Rift System – EARS; Chorowicz, 2005), cratons (e.g., Superior Craton, North China Craton, Kaapvaal Craton; Xu et al., 2018), and large igneous provinces (LIP; e.g., Paraná–Etendeka, Bushveld; Gomes and Vasconcelos, 2021). The currently considered scenarios of carbonatite genesis involve derivation from a volatile-rich mantle either by direct partial melting, extreme magmatic differentiation, or liquid immiscibility from CO₂-rich silicate melts (Guzmics et al., 2015; Weidendorfer et al., 2016), but these models still are evolving as a consequence of experimental work and natural observations. Carbonatite sources are thought to contain variable proportions of geochemically enriched mantle components as apparent from coupled Sr–Nd isotope systematics, overlapping with the field of ocean island basalt compositions (OIB; e.g., Bell and Simonetti, 2010; Iwamori and Nakamura, 2015) and towards Enriched Mantle I and II (EM I and EM II, respectively) end members. Besides their economic potential (e.g., Simandl and Paradis, 2018; Goodenough et al., 2021), carbonatite melts are thought to represent an important metasomatic agent in the upper mantle and subcontinental lithosphere (Coltorti et al., 1999; Kiseeva et al., 2013; Rudnick et al., 1993; Wallace and Green, 1988; Yaxley et al., 1991).

Among carbonatites, those with particularly unradiogenic ¹⁴³Nd/¹⁴⁴Nd ratios with $\epsilon_{\text{Nd}}(\text{i})$ (deviation from evolution line of the chondritic uniform reservoir; CHUR) values down to –18.3 and with a range of emplacement ages from ~2.0 Ga to 76 Ma have been reported from several regions, such as Paraná–Etendeka (Antonini et al., 2003) or South India (Ackerman et al., 2017; Kumar et al., 1998). The presence of these distinctive Nd isotope signatures also in coeval mantle-derived silicate rocks that are closely related to these carbonatites (e.g., kimberlites, nephelinites, lamprophyres, syenites; e.g., Ye et al., 2013; Comin-Chiaramonti et al., 2014; Ackerman et al., 2017; Sarmiento et al., 2021) may indicate that both rock types are derived from enriched mantle reservoir(s) with similarly low $\epsilon_{\text{Nd}}(\text{i})$ values. However, the ultimate nature of this unradiogenic ¹⁴³Nd/¹⁴⁴Nd signature remains unresolved. Recently, recycled crustal materials, such as marine carbonates, have been suggested to be present in the source of some carbonatites to account for their Sr–Nd–B–C–O–Mg isotope systematics (Amsellem et al., 2020; Cheng et al., 2017; Hoernle et al., 2002; Hulett et al., 2016; Song et al., 2017; Wang et al., 2021; Xu et al., 2018). Some other sources, such as depleted mantle hybridized by long-

term isolated Rb- and Nd-rich components, may be equally important for the peculiar chemical and isotope signatures of some carbonatites (e.g., Umbria-Latium Ultra-Alkaline District; Castorina et al., 2000), expanding a range of currently considered scenarios of the nature of carbonatite melts.

To provide further constraints on the potential source of carbonatites and various pathways of their formation throughout Earth's history, understand the possible processes responsible for generating the wide range of Sr–Nd–C–O isotope values recorded in carbonatites, and explore possible temporal connections of carbonatites and plate tectonics, we investigated several worldwide occurrences of carbonatites, with a range of emplacement ages spanning almost two billion years, and from diverse tectonic settings (continental rifts, hot-spots, traps, shear zones, post-collisional troughs, etc.), for radiogenic Sr–Nd and stable C–O isotope compositions, along with pertinent chemical and petrographic analyses. These new data are supplemented with published Sr–Nd–C–O isotope compositions of global carbonatites included in the GEOROC database (Sarbas and Nohl, 2008; Tab S1) to discuss their temporal, tectonic, and genetic variability.

2.2. Samples and analytical methods

Twenty-eight samples of carbonatites from 11 occurrences worldwide (Fig. 2.1) were examined in detail for petrography, mineralogy, abundances of major and trace elements, and Sr–Nd–C–O isotope compositions. The investigated carbonatite samples cover much of the petrographic (calcite/dolomite/ferruginous carbonatites) and chemical (REE-enriched/depleted, variable incompatible trace element patterns) variability, associations with a range of silicate rocks (syenites, phoscorites, etc.) known for global carbonatites (Woolley and Kjarsgaard, 2008a), and with emplacement ages ranging from ~2.06 Ga (Phalaborwa, South Africa) to ~40 Ma (Tororo and Sukulu; EARS). We refer to Tabs S1–S3 and Supplementary Text 1 for details on the individual carbonatite bodies examined in this study.

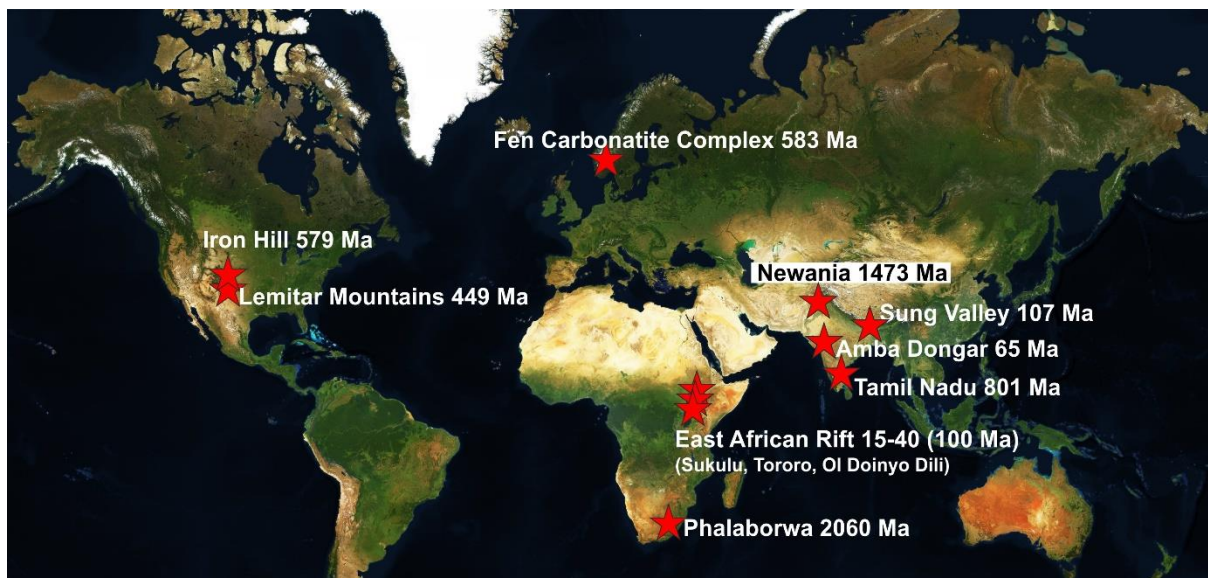


Fig. 2.1. Map of the occurrences of carbonatites sampled in this study together with their emplacement ages

For petrographic inspection, a JEOL JXA 8230 electron probe micro-analyzer (EPMA), housed at the Institute of Geology of the Czech Academy of Sciences (IG CAS) and equipped with an energy dispersive X-ray spectrometer (EDS), was employed. A FEG-SEM *Tescan Mira 3GMU* EPMA, housed at the Czech Geological Survey (CGS), was used for characterization of a subset of samples. For both instruments, the analyses were conducted with an accelerating voltage of 15 kV; a probe current beam of 10 nA was used at IG CAS whereas a 3 nA current beam was applied at CGS.

The whole-rock major element concentrations were determined at CGS or at the Faculty of Science, Charles University (Fén Complex), using conventional methods of wet analysis (Dempírová et al., 2010). The precision of the analyses was better than 5% (RSD) and the accuracy of the entire analytical protocol was monitored through repeat analyses of reference materials COQ-1 (carbonatite, USGS) and BCR-2 (basalt, USGS). Trace element contents for the majority of samples were obtained by employing an Agilent 7900x ICPMS, housed at CGS. A subset of samples was analyzed for trace elements using a Thermo *iCAP-Q*, housed at the Faculty of Science, Charles University in Prague. Reference materials BHVO-2 (basalt, USGS), JR-2 (rhyolite, GSJ), COQ-1, and JG-2 (granite, GSJ) were measured along with the unknown samples to monitor the accuracy and precision of the analytical protocols.

The stable C–O isotope compositions of carbonatites were determined using a *Delta V Advantage* IRMS, housed at CGS, following the analytical procedure given elsewhere (McCrea, 1950). Anhydrous 100% H₃PO₄ was added to the samples and allowed to react under vacuum for 24

hours at 22°C; dolomite was allowed to react for 72 hours under identical conditions. The results are reported in the conventional δ notation relative to V-SMOW for oxygen [$\delta^{18}\text{O} = ((^{18}\text{O}/^{16}\text{O}_{\text{sample}})/(^{18}\text{O}/^{16}\text{O}_{\text{V-SMOW}}) - 1) \times 1000$] and V-PDB for carbon [$\delta^{13}\text{C} = ((^{13}\text{C}/^{12}\text{C}_{\text{sample}})/(^{13}\text{C}/^{12}\text{C}_{\text{V-PDB}}) - 1) \times 1000$].

The Sr–Nd isotope compositions for the majority of samples were determined at IG CAS using the methods described in detail elsewhere (Ackerman et al., 2020). In brief, about 100–200 mg of a sample powder was dissolved in Savillex beakers using a mixture of 4 ml 14M HNO_3 and 1 ml 23M HF on a hot plate at 140 °C for at least 48 hours. The isolation of Sr and Nd from the matrix was performed following the methods given elsewhere (Pin et al., 2014). The procedure involved the addition of ascorbic acid to reduce Fe^{3+} to Fe^{2+} , followed by ion-exchange chromatography using the combination of Sr, TRU, and LN resins (Triskem Intl.). The Sr–Nd isotope compositions were determined using a *Triton Plus* thermal ionization mass spectrometer (Thermo Fisher Scientific). Strontium isotope analyses were performed using the single W filaments with Ta_2O_5 activator whereas Nd isotope measurements were done using a double-filament assembly with Re filaments. The external reproducibility of the measured $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios was monitored through the long-term analyses of NIST SRM 987 (Sr) and JNdi-1 (Nd) solutions that yield values of 0.710250 ± 5 (n=12) and 0.512099 ± 7 (n=10), respectively. Further control over the accuracy of the Sr–Nd isotope analyses were established through the long-term analyses of COQ-1 carbonatite reference material (USGS) with determined $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.703292 ± 14 (n=11) and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.512806 ± 9 (n=4).

The GCDkit software (Janoušek et al., 2006) was used for data handling and plotting.

2.3. Results

2.3.1 Petrography and mineralogy

The Phalaborwa carbonatites consist of calcite predominating over dolomite, abundant elongated idiomorphic apatite, randomly distributed together with large olivine grains with high forsterite contents (Giebel et al., 2017; Giebel et al., 2019 Fig. S1 a,b). Exsolution (“pseudo-graphic”) texture of high-temperature carbonatites with small oval worm-shaped dolomite enclosed in calcite was visualized using alizarin red (Fig. S1d). In most samples, olivine is the sole silicate phase. The humite-group mineral phases (probably chondrodite) were found in samples TCBwS1 and TCBwS3 in significant quantities (up to ca. 12 modal %). In samples BCBnoS2, TCBnoS1, TCBwS1, TCBwS2, and TCBwS3 variable amounts of fine-grained dispersed phlogopite (up to 5 modal %) were observed (Fig. S1c). Although abundant magnetite was reported in Phalaborwa carbonatites (Zaitsev et al.,

2014), in samples from this study it occurs rather scarcely as ~0.5 mm grains. Chalcopyrite lamellae in cubanite were observed in sample TCBws3 (Fig. S3a), and cobalto-pentlandite, covellite, and bornite were found in sample TCBws4 (Fig. S3b).

At Amba Dongar diatreme, the original phaneritic texture of magnetite-bearing calciocarbonatites is recrystallized to finer-grained carbonate grains and also silicified, to a variable extent, with the largest degree of silicification observed in sample IC40 (Fig. S1e). Calcite dominates over dolomite. The idiomorphic magnetite crystals are up to 2 cm large, and commonly weather out from the rocks at the outcrops. Quartz in this sample does not form phenocrysts, nor does it fill voids, but in the microcrystalline form, it corrodes carbonates along with crystal–grain boundaries.

Three samples of calciocarbonatites and one magnesiocarbonatite from Ol Doinyo Dili (Tanzania) contain abundant (3–7 modal %), up to 5 mm large phenocrysts of magnetite, associated with rare up to 3 mm large, slightly deformed phlogopite and idiomorphic apatite (Fig. S1f).

The phaneritic calciocarbonatites from the Fen carbonatite complex (samples CFN1, CFN2, CFN3, CFN8) are dominated by isometric calcite (~1–1.5 mm) with subordinate dolomite. Calciocarbonatites contain pyrite crystals, with decreasing frequency and size from CFN1 (Fig. S2a, S3c) to CFN2 and CFN3, and to CFN8 (pyrite-poor). Pyrite in sample CFN2 displays a brecciated structure with strong oxidation (hematitization) along cracks. Biotite is also present; it is most frequent in sample CFN3 (Fig. S2b), less frequent in CFN2 (1–2 mm, fragments of larger crystals), and rare in samples CFN1 and CFN8 (mostly 0.2 mm, occasionally ~1 mm). Sample CFN 1 contains columbite-(Fe) and pyrrhotite (Fig. S3c,d). Biotite has dispersed, cloudy margins. The rocks also contain abundant elongated apatite crystals. Except for CFN8, in which apatite does not exceed 0.3 mm, single crystals in other samples commonly reach ~2 mm. In CFN1 and CFN2, aggregates of parallel apatite crystals occur reaching ~1 cm in total length (Fig. S2c), and even larger apatite clusters were observed in sample CFN3. These apatite clusters show a strong preferred orientation of individual crystals, but the direction of preferred orientation varies along the cluster reaching several cm in length. Apart from primary idiomorphic crystals, secondary xenomorphic apatite filling up spaces between calcite grains was documented in sample CFN8. Carbonatite CFN9 (enriched in MgO compared to other calciocarbonatites from Fen) is fine-grained and contains accessory non-oxidized pyrite. The fine-grained groundmass contains ocelli of dolomite and fine-grained apatite (max. ~0.1 mm; Fig. S2d). No biotite was observed in this sample. Sample CFN7 (rödberg; hydrothermally altered iron-rich carbonatite) represents the extreme example of pyrite oxidation (Fig. S2e), observed in smaller amounts also in calciocarbonatites described above. Abundant pyrite (originally up to 4 mm large) decomposed to form large amounts of hematite, which infiltrated the entire rock along sub-grain boundaries in fully recrystallized calciocarbonatite and lending red color to the rock.

Petrography of Lemitar Mts., Iron Hill, Sukulu, and Tororo bodies has been detailed elsewhere (Ackerman et al., 2021; Benkó et al., 2021), whereas carbonatites from Sevattur were described in detail in Ackerman et al. 2017.

2.3.2 Major and trace element chemistry

Carbonatite samples from this study display a wide range of major element abundances (Tabs S1 and S2), and four different types can be distinguished using the different ternary plots (Woolley, 1982; Srivastava, 1993; Mitchell and Gittins, 2022; Fig. S4). Calciocarbonatites, characterized by the predominance of CaO over MgO/FeO^t ($n = 17$; Fig. S4), have variable but low FeO^t (0.01–7.9 wt. %), MgO (0.2–8.5 wt. %), and SiO₂ (0.01–3.9 wt. %) contents (Tab 2.1), and elevated P₂O₅ contents up to 6.2 wt. % due to high modal apatite. Magnesiocarbonatites ($n = 6$) have up to 16.2 wt. % MgO, dominated by Mg-carbonates (dolomite to Mg-calcite) and accessory Mg-silicate phases (e.g., phlogopite, olivine), whereas ferruginous carbonatites and rödberg ($n = 3$) show higher Fe₂O₃ over FeO (14–31 wt. % and 6–7 wt. %, respectively) due to the presence of large quantities of magnetite and/or hematite (case of rödberg). The silicified carbonatite (carbonatite affected by hydrothermal alteration with SiO₂-rich solutions) IC40 from Amba Dongar is distinguished by high SiO₂ (15.5 wt. %; Tab 1). The silicocarbonatites and silicified carbonatites are characterized by a wide range of SiO₂ contents (7.14–21.9 wt.%), and elevated Al₂O₃, TiO₂, Na₂O, and K₂O values due to abundant silicate phases (e.g., phlogopite, clinopyroxene, K-feldspar; Ackerman et al., 2021).

Tab. 2.1.

Major and trace element compositions

Sample	BCBnoS1	BCBnoS2	TCBno3	TCBno5	TCBws4	BCBws5	TCBno1	TCBws1	TCBws3
Locality	Phalaborwa	Phalaborwa	Phalaborwa	Phalaborwa	Phalaborwa	Phalaborwa	Phalaborwa	Phalaborwa	Phalaborwa
Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Fe-Carbonatite	Fe-Carbonatite	Fe-Carbonatite
SiO ₂ (wt%)	0.57	0.41	0.24	< 0.01	0.18	< 0.01	2.61	4.43	7.48
TiO ₂	0.13	0.24	0.03	0.04	0.08	0.03	0.03	0.07	0.31
Al ₂ O ₃	1.46	0.79	0.46	0.08	0.19	1.54	0.48	3.98	0.44
Fe ₂ O ₃	1.96	4.11	2.02	< 0.01	1.70	0.94	14.17	30.77	21.77
FeO	1.95	3.43	1.42	< 0.01	1.24	0.78	6.55	14.08	9.49
MgO	4.45	3.89	2.93	2.88	8.02	8.45	5.87	16.18	13.78
MnO	0.09	0.10	0.09	0.10	0.07	0.10	0.14	0.14	0.15
CaO	48.79	48.51	50.19	50.19	47.67	45.48	37.29	13.82	25.57
Na ₂ O	0.05	0.05	0.05	0.06	0.06	0.04	0.04	0.05	0.03
K ₂ O	0.03	0.02	0.02	0.02	0.03	< 0.01	0.05	0.43	0.25
P ₂ O ₅	6.16	5.21	3.03	0.25	0.43	0.79	0.11	0.77	1.67
F	0.32	0.31	0.17	0.02	0.17	0.09	0.05	0.44	0.45
S	0.02	0.03	0.02	< 0.010	1.07	0.75	0.13	2.18	1.41
CO ₂	32.67	31.76	37.87	42.83	39.59	40.99	30.47	13.57	17.95
H ₂ O+	0.93	0.75	0.58	1.43	< 0.05	< 0.05	0.96	< 0.05	< 0.05
H ₂ O-	0.07	0.08	0.05	0.06	0.06	< 0.05	0.06	< 0.05	< 0.05
Total	99.66	99.70	99.17	97.96	100.56	99.98	99.00	100.92	100.75
Li (ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sc	5.72	8.91	2.23	4.65	0.37	<0.01	11.30	60.9	26.3
V	38	98.9	23.6	2.1	3.3	<2	84.9	113	199
Cr	2.32	1.42	1.22	1.27	1.22	1.38	2.28	10.1	3.72
Co	23	40	16	4.1	53	219	68	100	51
Ni	32.2	63	27	5.4	142	246	55	173	30

	BCBnoS1	BCBnoS2	TCBno3	TCBno5	TCBws4	BCBws5	TCBno1	TCBws1	TCBws3
Cu	1211	45	1830	16	8242	7376	2107	13813	14064
Zn	80	117	131	136	46	49	97	185	126
Ga	14	12	10.8	8.5	12	15	9.1	21	14
Rb	0.47	0.8	0.61	1.1	0.66	0.54	1.8	24	11
Sr	5000	4343	5281	5283	4440	5515	3536	2420	3840
Y	90	70	84	78	84	87	48	33	51
Nb	3.6	3.6	1.4	0.4	4.0	0.9	8.8	27	13.1
Zr	143	123	123	5.7	74	39	202	200	1562
Cd	0.10	0.81	0.13	0.15	0.16	0.29	0.23	0.56	0.82
Cs	<0.1	0.26	0.27	0.23	0.18	0.25	0.21	0.45	0.37
Ba	514	661	924	933	189	186	407	706	561
La	286	215.6	235	210	257	337	116	149	174
Ce	825	596.2	657	566	729	960	329	398	460
Pr	89	77.9	84	73	84	104	44	51	57
Nd	463	321.3	351	297	421	490	182	208	228
Sm	79	56	60	52	69	87	32	33	38
Eu	17	13	14.2	12.6	11.4	14.3	8	5.9	8.9
Gd	58	42.3	46	41	46	58	25	22	28
Tb	6.0	4.3	4.9	4.3	4.8	5.9	2.7	2.2	3.0
Dy	20.2	15.2	18	16	17	20	10	7.3	11
Ho	2.7	2.1	2.5	2.2	2.5	2.7	1.4	0.98	1.5
Er	4.9	3.8	4.6	4.3	4.7	4.9	2.7	1.77	2.8
Tm	0.42	0.33	0.41	0.39	0.44	0.44	0.25	0.16	0.26
Yb	2.17	1.75	2.18	2.10	2.37	2.36	1.30	0.85	1.59
Lu	0.27	0.21	0.27	0.27	0.30	0.30	0.16	0.10	0.19
Hf	1.88	2.19	1.74	0.20	0.80	0.50	3.3	3.1	23
Ta	0.25	0.34	0.18	0.05	0.70	0.14	0.84	1.94	1.23
Pb	7.2	6.1	4.2	21	33	30	5.2	26	26
Th	16	6.2	5.6	2.3	78	34	1.6	66	16
U	4.2	0.91	0.76	0.23	19	16	0.75	18	8.7
Tl	0.06	0.06	0.01	0.05	0.15	0.12	0.10	0.09	0.12
W	0.32	0.25	0.28	0.21	0.30	7.6	0.31	0.34	0.32

Tab. 2.1.

Continued

Sample	TCBws2	TCBws5	NE9	NE19	SUNG9	IC41A	IC41B	IC42	17AM5
Locality	Phalaborwa	Phalaborwa	Newania	Newania	Sung Valley	Amba Dongar	Amba Dongar	Amba Dongar	Amba Dongar
Carbonatite	Mg-Carbonatite	Mg-Carbonatite	Mg-Carbonatite	Mg-Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Ca-Carbonatite
SiO ₂ (wt%)	0.12	1.65	0.82	0.22	0.46	3.52	0.42	3.94	1.47
TiO ₂	0.12	0.12	0.03	0.08	0.11	0.36	0.04	0.03	0.31
Al ₂ O ₃	0.22	0.29	0.31	0.03	0.19	0.59	0.15	0.13	0.15
Fe ₂ O ₃	1.56	3.61	< 0.01	< 0.01	0.39	8.58	0.35	1.86	5.36
FeO	0.93	2.94	11.71	11.50	0.84	0.13	0.15	0.14	0.43
MgO	11.24	14.05	13.16	16.10	2.59	0.24	0.35	0.52	1.39
MnO	0.09	0.11	0.80	0.78	0.12	0.32	0.16	0.25	0.18
CaO	45.99	39.26	29.44	24.44	51.59	47.01	54.47	51.28	46.83
Na ₂ O	0.04	0.04	0.11	0.02	0.05	0.08	0.07	0.04	0.06
K ₂ O	0.03	0.07	0.12	< 0.01	0.05	0.03	0.01	0.04	0.03
P ₂ O ₅	0.56	3.60	1.28	0.27	0.09	0.78	0.15	0.64	2.35
F	0.13	0.44	0.14	0.05	< 0.01	0.16	0.08	0.17	0.17
S	1.57	0.79	< 0.010	0.01	< 0.010	0.04	< 0.010	0.02	< 0.010
CO ₂	38.90	31.92	39.36	36.75	42.40	37.18	43.05	41.14	37.35
H ₂ O+	< 0.05	< 0.05	1.41	4.99	0.31	0.32	< 0.05	< 0.05	0.22
H ₂ O-	< 0.05	0.08	< 0.05	< 0.05	< 0.05	0.06	0.07	0.06	0.05
Total	101.49	98.97	98.70	95.24	99.20	99.39	99.53	100.26	96.35
Li (ppm)	nd	nd	nd	nd	<0.01	3.5	1.57	3.3	<0.01
Sc	0.76	8.55	<0.01	19	7.7	<0.01	<0.01	1.1	<0.01
V	<2	35	36	8.9	24	346	25	193	197
Cr	1.31	1.77	13	58	0.28	<1	<1	0.27	<1
Co	106	64	29	42	3.3	2.3	1.9	3.0	13
Ni	167	119	6.2	24	3.7	0.64	0.75	0.9	2.7

	TCBws2	TCBws5	NE9	NE19	SUNG9	IC41A	IC41B	IC42	17AM5
Cu	9231	6189	12	95	<1	1.8	2.2	6	12
Zn	38	64	46	16	39	176	3.9	26	216
Ga	14	16	4.0	2.1	5.4	6.5	3.4	3.1	10.5
Rb	1.3	3.3	16	0.48	1.5	1.2	0.7	1.8	1.9
Sr	5956	4262	8130	2454	4052	1864	6407	3724	5499
Y	89	59	22	11	62	27	27	62	76
Nb	2.1	10.7	114	1494	13	734	401	437	441
Zr	52	224	7.74	19	37	2.10	0.51	1.37	204
Cd	0.36	0.16	0.98	0.21	0.17	0.47	0.23	0.35	0.33
Cs	0.44	0.46	0.27	0.27	0.46	0.06	<0.1	0.08	0.36
Ba	221	329	102	21	211	3332	1306	2191	1297
La	314	295	91.6	55	138	495	314	276	309
Ce	893	862	239	118	371	984	590	555	744
Pr	97	95	30	12.3	45	98	54	51	78
Nd	495	486	119	43	173	327	175	168	263
Sm	83	77	18.9	6.6	27	40	23	24	34
Eu	14	13	5.19	1.8	8	10	6.2	6.8	8.8
Gd	54	49	14.9	5.6	23	27	17	19	29
Tb	5.5	4.6	1.67	0.7	2.8	3.1	2.04	2.6	3.2
Dy	18	14	6.01	2.8	12	13	8	13	13
Ho	2.5	1.9	0.82	0.42	1.9	2.2	1.60	2.9	2.4
Er	4.7	3.2	1.60	0.9	4.3	4.5	3.6	7.3	5.6
Tm	0.43	0.28	0.16	0.09	0.45	0.52	0.49	1.2	0.66
Yb	2.27	1.47	0.85	0.56	2.6	2.8	2.7	7.2	4.3
Lu	0.27	0.17	0.1	0.08	0.32	0.43	0.42	1.1	0.58
Hf	0.59	2.99	0.23	0.64	0.60	0.05	0.05	0.09	3.66
Ta	0.90	0.74	22.7	41	1.1	0.46	4.9	2.1	21
Pb	20	405	40.5	79	2.8	48	11	15	24
Th	37	1036	1.53	0.96	0.17	0.09	0.07	0.35	86
U	11	237	18	34	0.11	0.91	4.5	2.12	61
Tl	0.12	0.28	0.15	0.18	0.11	0.03	0.03	0.19	0.14
W	0.30	0.27	0.38	0.87	0.23	5	0.7	2.47	2.93

Tab. 2.1.
Continued

Sample	IC40	AC05A	AC05B	AC05C	CFN1	CFN2	CFN3	CFN8	CFN7	CFN9
Locality	Amba Dongar	Ol Doinyo Dili	Ol Doinyo Dili	Ol Doinyo Dili	Fen Carbonatite Complex	Fen Carbonatite Complex	Fen Carbonatite Complex	Fen Carbonatite Complex	Fen Carbonatite Complex	Fen Carbonatite Complex
Carbonatite	Silificied carbonatite	Ca-Carbonatite	Ca-Carbonatite	Mg-Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Ca-Carbonatite	Rödberg	Mg-Carbonatite
SiO ₂ (wt%)	15.52	< 0.01	< 0.01	0.13	0.62	0.66	0.90	0.50	2.84	0.96
TiO ₂	0.32	0.10	0.24	0.02	0.09	0.01	0.01	< 0.01	0.05	0.03
Al ₂ O ₃	1.10	0.17	0.19	0.25	0.08	0.21	0.40	0.18	0.98	0.32
Fe ₂ O ₃	13.65	2.31	5.14	2.13	3.02	0.70	1.17	1.84	17.48	2.18
FeO	< 0.01	1.72	2.29	0.70	1.62	0.55	0.63	0.37	3.27	3.52
MgO	1.10	3.33	0.31	14.06	1.25	3.29	3.24	3.01	0.89	7.43
MnO	1.48	0.37	0.82	0.53	0.31	0.31	0.29	0.28	0.38	1.07
CaO	35.33	50.47	54.12	36.79	50.15	50.04	49.08	50.72	38.86	41.55
Na ₂ O	0.11	0.10	0.12	0.07	0.04	0.05	0.07	0.03	0.32	0.07
K ₂ O	0.02	0.22	0.27	0.13	0.06	0.16	0.26	0.14	0.03	0.05
P ₂ O ₅	3.18	3.99	1.14	0.63	0.98	1.78	3.72	1.95	0.37	0.40
F	0.06	0.24	0.14	0.06	nd	nd	nd	nd	nd	nd
S	0.09	< 0.010	0.01	< 0.010	0.50	0.09	0.28	0.11	2.15	0.15
CO ₂	24.55	35.89	34.10	44.46	40.06	41.23	38.53	39.80	30.49	39.92
H ₂ O+	0.61	0.51	0.55	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.06	< 0.05
H ₂ O-	0.15	0.09	0.09	0.08	0.08	0.12	< 0.05	0.14	0.18	0.14
Total	97.26	99.53	99.54	100.05	98.86	99.20	98.62	99.07	98.35	97.79
Li (ppm)	8	3	5.7	1.79	0.80	0.02	0.9	0.19	1.35	5.8
Sc	2.2	12	<0.01	<0.01	<0.01	3.4	2	<0.01	70.5	10.5
V	758	28	297	7.7	182	49	<2	<2	23	1.71
Cr	<1	2	0.99	<1	<1	<1	<1	<1	25	<1
Co	2.0	9.9	2.71	11	5.2	0.55	9.7	4.64	7.91	7.05
Ni	0.29	3.7	0.68	1.14	16	1.64	34	14	19	11

	IC40	AC05A	AC05B	AC05C	CFN1	CFN2	CFN3	CFN8	CFN7	CFN9
Cu	16	1.8	<1	1.15	3.05	<1	20	2.59	3.62	3.25
Zn	2062	82	1414	18	30	3.34	22	7	47	26
Ga	17	7.5	10.3	1.1	nd	nd	nd	nd	nd	nd
Rb	0.57	0.88	6.34	1.5	2.3	0.91	6.9	3.3	0.77	0.99
Sr	3211	3299	3979	1717	5981	914	4663	4942	519	1266
Y	115	65	33	4	39	66	68	61	190	30
Nb	1028	264	789	247	585	111	206	30	525	142
Zr	0.44	46	1.92	0.22	57	48	50	23	130	56
Cd	0.42	0.4	21	0.33	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cs	0.04	<0.1	0.17	0.05	0.07	<0.1	0.23	0.05	0.13	0.15
Ba	8393	900	2132	117	412	896	945	568	200	384
La	1565	363	423	36	147	252	289	251	3149	4147
Ce	3037	815	926	60	328	525	626	507	6426	6005
Pr	289	91	101	8.7	36	59	71	58	756	640
Nd	930	339	366	33	128	213	260	213	2710	2305
Sm	117	52	47	5.2	21	35	43	35	334	253
Eu	31	15	12.5	1.5	5.8	10	12	9.8	70	37
Gd	85	38	30	3.9	17	29	35	27	186	103
Tb	9.8	4.7	3.4	0.5	2.3	3.9	4.5	3.7	19.8	10.9
Dy	38	19.3	13	2	9.4	16	18	15	43	9.5
Ho	6.4	3.4	2.2	0.37	1.6	2.7	2.9	2.5	6.7	1.3
Er	12.4	6.8	4.2	0.73	3.9	7.0	7.0	6.3	16	2.8
Tm	1.4	0.78	0.41	0.08	0.50	0.87	0.89	0.8	2.1	0.35
Yb	6.5	3.8	1.8	0.4	3.2	5.5	5.7	5.2	14	2.9
Lu	0.88	0.52	0.23	0.06	0.46	0.80	0.82	0.75	2.1	0.44
Hf	0.08	1.03	<0.50	<0.50	1.3	0.77	<0.50	<0.50	2.4	<0.50
Ta	0.18	9.3	<0.50	1.3	<0.50	6.6	8.6	1.04	<0.50	<0.50
Pb	618	17	27	<0.1	7.4	15	21	14	40	26
Th	0.06	15	0.17	<0.1	14	87	195	51	1573	297
U	1.88	10.1	2.7	0.98	0.35	13	30	19	4.6	43
Tl	0.03	<0.1	0.15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
W	3.02	0.13	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Tab. 2.1. Major and trace element compositions of carbonatites; nd - not detected

The systematics of rare earth elements (REE) and other trace elements exhibit features characteristic of carbonatites, such as LREE enrichment, with variable depletions/enrichments in Th, U, Nb, and Ta, closely related to mineralogy, reflecting cumulation of magmatic and post-magmatic processes. Among the observed anomalies, pronounced Zr–Hf depletions rise above others in the carbonatites (Fig. S5). The Nb–Ta distribution shows extreme variation, which is related to the variable modal abundance of pyrochlore (e.g., Newania pyrochlore-rich carbonatites show Nb_N/La_N up to 26.7). The sum of REE contents (ΣREE) varies by almost three orders of magnitude from 33 to ~13,700 ppm with the highest ΣREE values found in rödberg CFN7 and magnesiocarbonatite CFN9 from Fen. These two samples display very high La_N/Yb_N ratios of 148 and 977, respectively. Elevated La_N/Yb_N ratios have also been found for ferruginous carbonatite TCBws1 and Mg-rich carbonatite TCBws5 (both Phalaborwa) with La_N/Yb_N of 119 and 137, respectively. Carbonatite samples from Phalaborwa, Newania, Amba Dongar, Sung Valley, and Ol Doinyo Dili are characterized by broadly similar LREE-enriched patterns with La_N/Yb_N values from 25 to 97 (Supplementary Text 1). Partly silicified calciocarbonatite IC41A from Amba Dongar and calciocarbonatite AC05B from Ol Doinyo Dili yield La_N/Yb_N of 121 and 164, respectively. Samples from the Fen Complex and most of the Amba Dongar calciocarbonatites have less steep HREE profiles ($Dy_N/Yb_N \sim 1.2\text{--}2.1$) compared to the rest of the carbonatites (3.0–6.4). Magnesiocarbonatites and Fe-rich carbonatites generally have higher contents of compatible elements (Co, Ni, Cr) than calciocarbonatites. The Phalaborwa carbonatites are significantly enriched in Cu due to late-stage Cu mineralization. In calciocarbonatites, Zr depletion is generally more pronounced than Hf depletion compared to magnesiocarbonatites and Fe-rich carbonatites.

2.3.3 Radiogenic Sr–Nd isotope systematics

The radiogenic Sr–Nd isotope compositions of carbonatites from this study are plotted in Fig. 2.2 and listed in Tab 2.2, along with Rb, Sr, Sm, and Nd concentrations. Most samples have Rb contents typically <2 ppm, and generally high Sr >3,000 ppm, with $^{87}Rb/^{87}Sr < 0.001$, leading to negligible changes in the age-corrected $^{87}Sr/^{86}Sr(i)$ values. Samarium and Nd contents range from 5.2 to 117 ppm and 33 to 930 ppm, respectively, with $^{147}Sm/^{144}Nd$ ratios between 0.074 and 0.107. Two most REE-enriched carbonatites CFN9 and CFN7 (Fen) exhibit high Sm and Nd abundances (>253 ppm and >2,305 ppm, respectively) but their $^{147}Sm/^{144}Nd$ ratios do not depart significantly from the range reported above. No correlation was found between bulk-rock major/trace elements or Sr–Nd isotope composition of carbonatites and geotectonic settings or geographic provenance.

Tab. 2.2 Rb-Sr, Sm-Nd and C-O isotopic ratios for carbonatites

Sample	Locality	Carbonatite	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$	$\varepsilon_{\text{Sr}(i)}$	Nd (ppm)	Sm (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}_{(i)}$	$\varepsilon_{\text{Nd}(i)}$	$\delta^{13}\text{C}$ (‰ PDB)	$\delta^{18}\text{O}$ (‰ SMOW)
BCBnoS1	Phalaborwa	Ca-carbonatite	0.47	5000	0.0003	0.705702 ± 10	0.7057	52	463	79	0.103	0.511209 ± 06	0.50981	-3.4	-3.7	8.8
BCBnoS2	Phalaborwa	Ca-carbonatite	0.81	4343	0.001	0.705524 ± 08	0.7055	49	321	56	0.105	0.511216 ± 04	0.50980	-3.7	-2.6	8.6
TCBno3	Phalaborwa	Ca-carbonatite	0.61	5281	0.0003	0.705406 ± 07	0.7054	48	351	60	0.104	0.511209 ± 04	0.50981	-3.6	-3.4	8.2
TCBno5	Phalaborwa	Ca-carbonatite	1.11	5283	0.001	0.705634 ± 07	0.7056	51	297	52	0.106	0.511227 ± 05	0.50980	-3.7	-2.6	9.0
TCBws4	Phalaborwa	Ca-carbonatite	0.66	4440	0.0004	0.704108 ± 08	0.7041	29	421	69	0.099	0.511238 ± 07	0.50991	-1.5	-4.5	8.8
BCBws5	Phalaborwa	Ca-carbonatite	0.54	5515	0.0003	0.704465 ± 08	0.7045	34	490	87	0.107	0.511184 ± 04	0.50974	-4.8	-4.5	8.8
TCBno1	Phalaborwa	Fe-carbonatite	1.79	3536	0.001	0.705326 ± 10	0.7053	46	182	32	0.106	0.511236 ± 04	0.50980	-3.7	-3.5	8.6
TCBws1	Phalaborwa	Fe-carbonatite	24.1	2420	0.029	0.705678 ± 09	0.7048	40	208	33	0.095	0.511149 ± 05	0.50987	-2.4	-4.2	9.1
TCBws3	Phalaborwa	Fe-carbonatite	11.1	3840	0.008	0.706162 ± 09	0.7059	55	228	38	0.100	0.511149 ± 05	0.50980	-3.7	-3.8	9.0
TCBws2	Phalaborwa	Mg-carbonatite	1.29	5956	0.001	0.704054 ± 06	0.7040	28	495	83	0.101	0.511208 ± 11	0.50985	-2.7	-4.6	8.3
TCBws5	Phalaborwa	Mg-carbonatite	3.31	4262	0.002	0.704459 ± 08	0.7044	33	486	77	0.096	0.511149 ± 05	0.50986	-2.5	-3.9	8.6
NE9	Newania	Mg-carbonatite	16.3	8130	0.006	0.702163 ± 08	0.7020	-10	125	20	0.095	0.511564 ± 08	0.51064	-1.9	-4.7	9.4
NE19	Newania	Mg-carbonatite	0.48	2454	0.001	0.702501 ± 08	0.7025	-3.7	43	6.6	0.092	0.511477 ± 06	0.51059	-2.9	-4.5	10.4
SUNG9	Sung Valley	Ca-Carbonatite	1.53	4052	0.001	0.704773 ± 08	0.7048	5.6	173	27	0.096	0.512564 ± 04	0.51256	1.2	-2.9	7.4
IC41A	Amba Dongar	Ca-Carbonatite	1.17	1864	0.002	0.705790 ± 10	0.7058	19	327	40	0.074	0.512482 ± 04	0.51248	-1.4	-3.1	12.0
IC41B	Amba Dongar	Ca-Carbonatite	0.65	6407	0.0003	0.705555 ± 11	0.7056	16	175	23	0.078	0.512501 ± 05	0.51250	-1.0	-4.4	9.0
IC42	Amba Dongar	Ca-Carbonatite	1.83	3724	0.001	0.705741 ± 09	0.7057	19	168	24	0.086	0.512469 ± 05	0.51247	-1.7	-4.5	10.7
17AM5	Amba Dongar	Ca-Carbonatite	1.93	5499	0.001	0.705409 ± 09	0.7054	14	263	34	0.078	0.512506 ± 04	0.51251	-1.0	-4.4	10.2
IC40	Amba Dongar	Silificied carbonatite	0.57	3211	0.001	0.705727 ± 09	0.7057	19	930	117	0.076	0.512495 ± 05	0.51250	-1.2	-3.4	13.8
AC05A	Ol Doinyo Dili	Ca-Carbonatite	0.88	3299	0.001	0.703211 ± 07	0.7032	-18	339	52	0.093	0.512787 ± 05	0.51279	2.9	-3.0	15.6
AC05B	Ol Doinyo Dili	Ca-Carbonatite	6.34	3979	0.005	0.704341 ± 08	0.7043	-2.2	366	47	0.077	0.512647 ± 05	0.51265	0.2	-3.1	8.7
AC05C	Ol Doinyo Dili	Mg-Carbonatite	1.53	1717	0.003	0.703135 ± 09	0.7031	-19	33	5.2	0.095	0.512784 ± 06	0.51278	2.9	-2.5	18.3
CFN1	Fen Carbonatite C.	Ca-Carbonatite	2.26	5981	0.001	0.702956 ± 09	0.7029	-12	128	21	0.101	0.512444 ± 05	0.51206	3.4	-4.8	7.4
CFN2	Fen Carbonatite C.	Ca-Carbonatite	0.91	914	0.003	0.703063 ± 09	0.7030	-11	213	35	0.100	0.512423 ± 05	0.51204	3.1	-4.9	7.2
CFN3	Fen Carbonatite C.	Ca-Carbonatite	6.94	4663	0.004	0.703101 ± 05	0.7031	-11	260	43	0.099	0.512430 ± 07	0.51205	3.2	-4.9	7.4
CFN8	Fen Carbonatite C.	Ca-Carbonatite	3.32	4942	0.004	0.703024 ± 06	0.7030	-11	213	35	0.075	0.512416 ± 05	0.51204	3.0	-3.4	9.0
CFN7	Fen Carbonatite C.	Rödberg	0.77	519	0.002	0.710404 ± 04	0.7104	93	2710	334	0.098	0.512363 ± 05	0.51208	3.7	-4.9	7.2
CFN9	Fen Carbonatite C.	Mg-Carbonatite	0.99	1266	0.002	0.705404 ± 06	0.7054	22	2305	253	0.066	0.512335 ± 05	0.51208	3.8	-2.7	8.0

Tab. 2.2. Rb-Sr, Sm-Nd, and C-O isotopic ratios for carbonatites in this study. $\varepsilon_{\text{Sr}(i)}$ is defined as $^{87}\text{Sr}/^{86}\text{Sr}(i) / ^{87}\text{Sr}/^{86}\text{Sr}(i) (\text{CHUR}) - 1) \times 10,000$; $\varepsilon_{\text{Nd}(i)}$ is defined as $^{143}\text{Nd}/^{144}\text{Nd}(i) / ^{143}\text{Nd}/^{144}\text{Nd}(i)(\text{CHUR}) \times 10,000$.

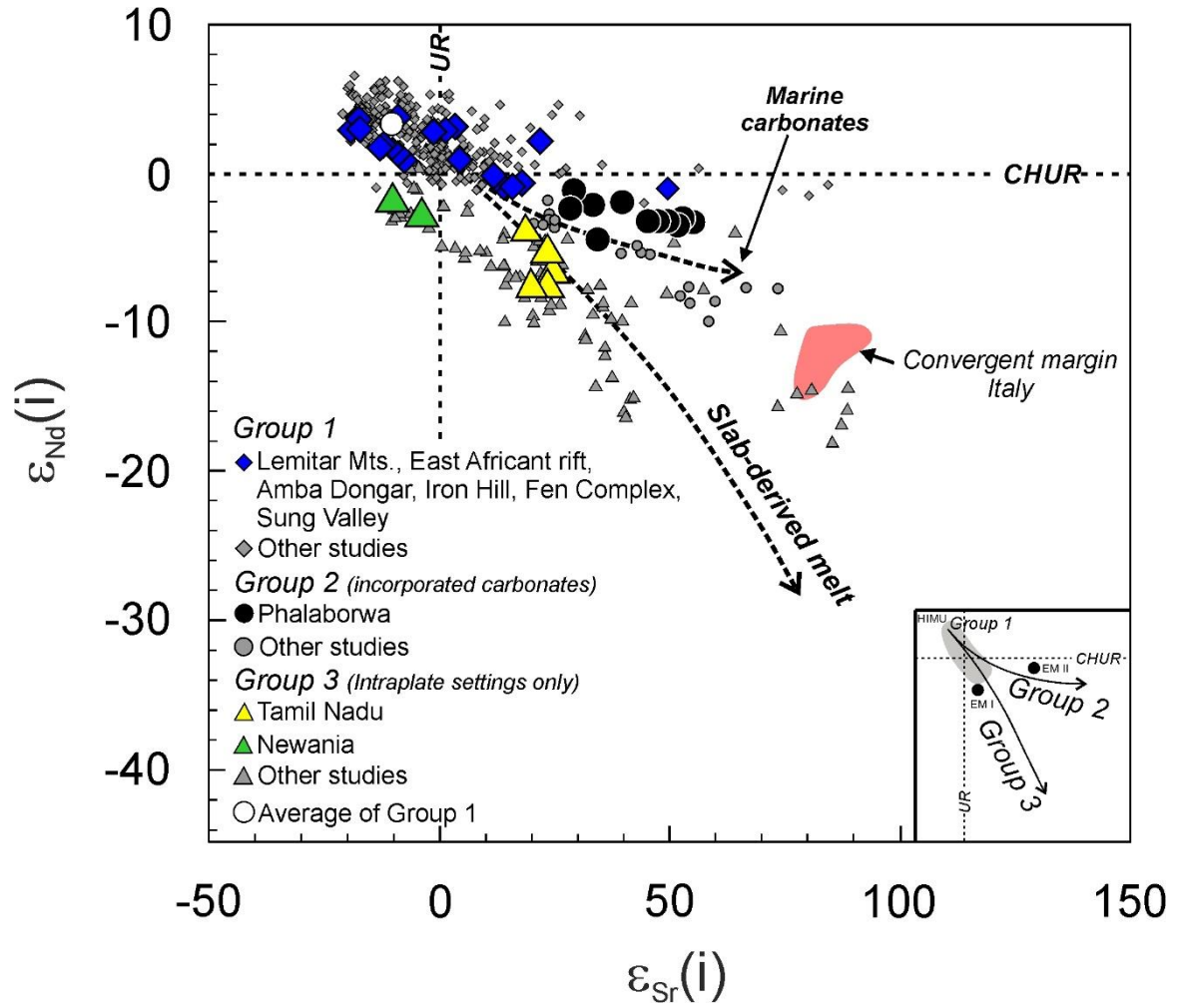


Fig. 2.2. Sr–Nd isotope systematics of global carbonatites plotted as $\epsilon_{\text{Nd}}(i)$ vs $\epsilon_{\text{Sr}}(i)$ values. **Group 3** with a steep slope suggests the derivation from an ancient, enriched mantle source whereas the shallow **Group 2** can be attributed to the involvement of recycled marine carbonates (see the discussion for more details). Details on the source of data are given in Supplementary Text 2. Bigger symbols are samples analyzed in this study. Values of EM I, EM II and an average of Group 1 carbonatites are given in the Supplementary text. $\epsilon_{\text{Sr}}(i)$ is defined as $\epsilon_{\text{Sr}}(i) = \left(\frac{^{87}\text{Sr}/^{86}\text{Sr}(i)}{^{87}\text{Sr}/^{86}\text{Sr}(\text{CHUR})} - 1 \right) \times 10,000$; $\epsilon_{\text{Nd}}(i)$ is defined as $\epsilon_{\text{Nd}}(i) = \left(\frac{^{143}\text{Nd}/^{144}\text{Nd}(i)}{^{143}\text{Nd}/^{144}\text{Nd}(\text{CHUR})} - 1 \right) \times 10,000$.

The high abundances of Th and U, from 0.02 to 1,573 and from 0.11 to 630 ppm, respectively, and relatively high Pb contents from 2.83 to 618 ppm in whole-rock samples (Tab 2.1), lead to some extremely variable radiogenic measured $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values (for example, Phalaborwa magnesiocarbonatite TCBws5 has $^{208}\text{Pb}/^{204}\text{Pb}$ of ~7,132; unpublished data); the same also applies to recalculated initial ratios. It is unclear whether these variable but high abundances of Pb, Th, and U are primary or if they originated through some secondary process, such as late-stage hydrothermal alteration or Pb loss (Rukhlov and Bell, 2010). For these reasons, we do not report Pb isotope data.

2.3.4 Stable C–O isotope compositions

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of carbonatites from this study are listed in Tab 2.2 and plotted in Fig. S3. They vary from 7.2 to 18.3‰ and between –4.9 and –2.5‰, respectively (Tab 2.2, Fig. 2.3, S6, S9). All new data are within the range of C–O isotope compositions of global carbonatites whose variations were variously ascribed to derivation from mantle sources or resulting from hydrothermal/meteoric water alteration, metamorphism, mixing with sedimentary carbonate, and occasionally to incorporation of organic carbon. Most samples plot in the field of primary igneous carbonatites (Ray and Ramesh, 2006), with some samples plotting at the boundary to the mantle field of Kyser, 1990. Magnesiocarbonatites always display higher $\delta^{13}\text{C}$ than coexisting calciocarbonatites from the same locality (Fen, Ol Doinyo Dili), consistent with observations from natural systems and attesting to equilibrium C isotope fractionation (e.g., Schwarcz, 1966; Sheppard and Schwarcz, 1970; Ray et al., 1999). Samples from Ol Doinyo Dili extend to high $\delta^{18}\text{O}$ (up to 18.3‰) and elevated $\delta^{13}\text{C}$ (up to –2.5‰), pointing to infiltration of meteoric water or hydrothermal alteration, or mixing with sedimentary carbonate.

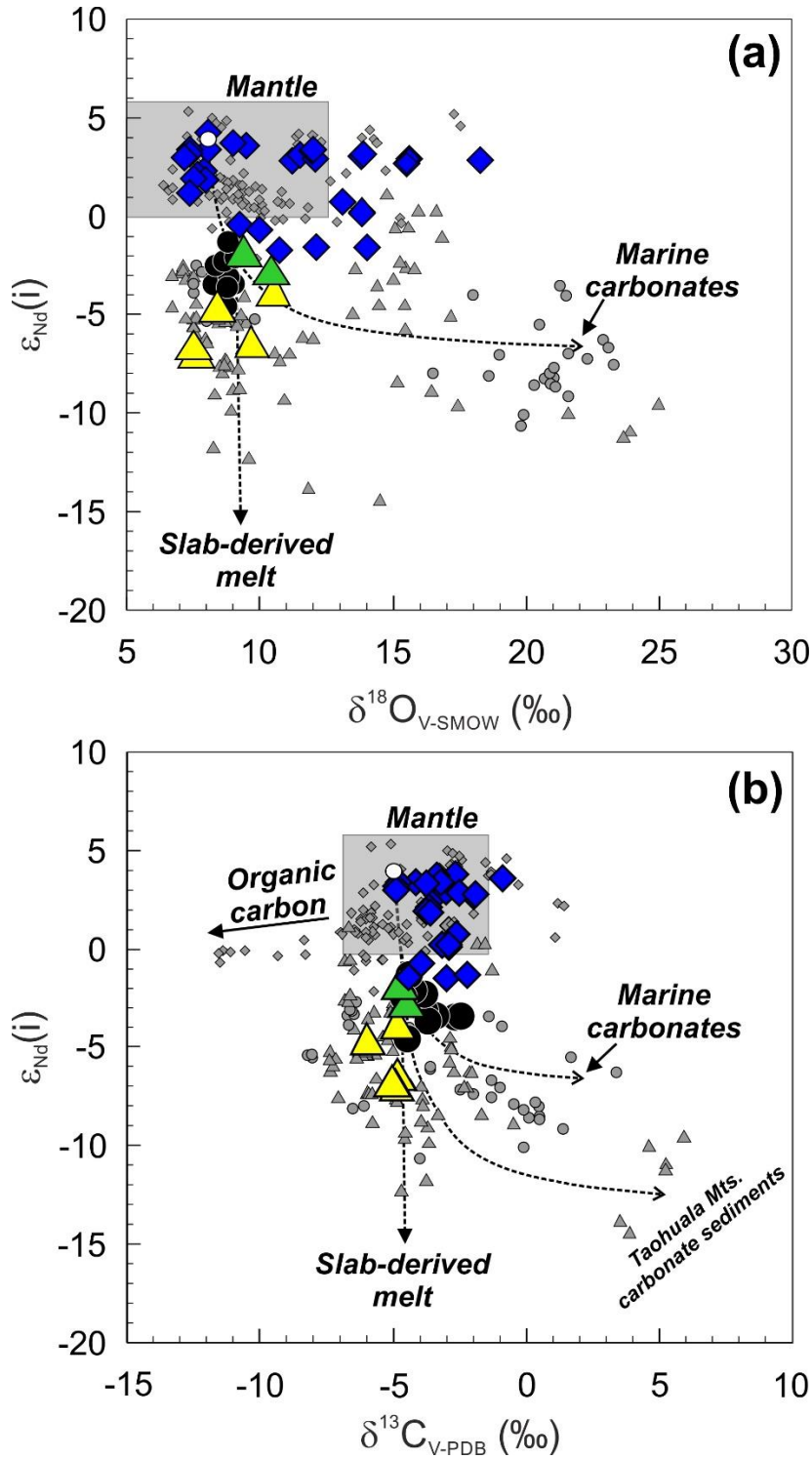


Fig. 2.3. Oxygen (a) and carbon (b) isotope variations versus $\epsilon_{Nd}(i)$ values recognized in the studied (colored large symbols) samples, global carbonatites (grey symbols), and Earth's mantle (Kyser, 1990). Largely positive $\delta^{18}O$ and $\delta^{13}C$ values paralleled by negative $\epsilon_{Nd}(i)$ signatures observed in many carbonatites are ascribed to the presence of variable amounts of recycled marine carbonates in the source sediments (e.g., Song et al., 2017; Xu et al., 2018; Wang et al., 2021) while largely negative $\delta^{13}C$ values indicate the presence of organic carbon (Woodard and Huhma, 2015). On the other hand, the carbonatites of **Group 3** in $\epsilon_{Nd}(i)$ – $\epsilon_{Sr}(i)$ (see Fig. 2.2 and chapter 2.4.4.) have mantle-like C–O isotope compositions. Note, that array for slab-derived melt and possible incorporation of marine carbonates are only tentative as the exact C–O isotope composition of both end members cannot be accessed. Symbols as in Fig. 2.2.

2.4. Discussion

Carbonatite magmas can originate either directly by low degree partial melting of CO₂-rich mantle lithologies, such as metasomatized (carbonated) peridotite/eclogite or regions with a high proportion of CO₂-rich recycled oceanic crust, or through liquid immiscibility from carbonated silicate melts at crustal levels (e.g., Woolley, 1989a; Dasgupta et al., 2004; Dasgupta et al., 2013; Jones et al., 2013). However, as recently suggested by (Yaxley et al., 2022), the majority of carbonatites are essentially cumulate rocks crystallized from calcitic–dolomitic melts or formed by silicate–carbonate liquid immiscibility from highly fractionated alkaline silicate melts. Furthermore, late-stage hydrothermal alteration and/or recrystallization of carbonatites are commonly associated with large-scale mobility of some elements (notably REE, U, Nb, etc.). Therefore, bulk-rock major/trace element systematics of carbonatites cannot be directly linked to the sources of carbonatite melts as they reflect a number of consecutive processes while the isotope systematics can potentially reflect the composition of primary, mantle-derived sources.

2.4.1. Sr–Nd–C–O isotope systematics of carbonatites: Primary versus secondary signature?

Before the possible linkage of Sr–Nd–C–O isotope systematics of carbonatites to mantle sources is established, there is a need to critically evaluate whether late-stage processes can be responsible for some of the extreme variations of Sr–Nd–C–O isotope compositions reported for global carbonatites (Figs. 1 and 2). This is particularly important because carbonatites are prone to large-scale, late-stage co-magmatic and/or hydrothermal/carbothermal overprint and mineralization, which often modify the elemental budgets of Ba, Sr, REE, U, Th, and Nb (e.g., Doroshkevich et al., 2009; Giebel et al., 2017; Marien et al., 2018; Magna et al., 2020; Benkó et al., 2021). By inference, these processes also may, in opportune situations, disturb or completely erase the original Sr–Nd–C–O isotope signatures of carbonatites. To understand the possible influence of late-stage modifications on the Sr–Nd–C–O isotope systematics of carbonatites, we focused in detail on two carbonatite bodies investigated in this study, the Lemitar Mts. (USA; Fig. 4 a-e, h) and Fen Complex (Norway Fig. 4 f, g), that show clear signs of post-emplacement perturbations and can therefore serve as a proxy for global signatures of post-emplacement remobilization.

In the case of the Lemitar Mts., the extent of recrystallization, secondary filling of amygdaloids, and even the degree of silicification (increasing SiO₂ contents in the trend UC08 → UC03A → UC04 → UC07A → UC02; Tab 2.1 and Fig. S4) correlate well with increasing Rb/Sr ratios and increasingly more radiogenic ⁸⁷Sr/⁸⁶Sr(i) values. The Rb–Sr isotope system is known to be susceptible to hydrothermal alteration (e.g., Andersen, 1987; Andrade et al., 1999; Kawahata et al., 2001) although

such an effect may, at first sight, be less apparent in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios due to generally high Sr contents in carbonatites (up to ~8,000 ppm; Tab 2.2). However, both carbonatite suites examined here (Lemitar Mts., Fen) exhibit decoupled Sr–Nd isotope systematics (horizontal array in the Sr–Nd plot; Fig. 2.2). This trend could be explained by (i) post-magmatic Rb loss (underestimated correction for ^{87}Rb) which is unlikely given the very low Rb contents, Rb/Sr ratios typically $\ll 0.01$ and, by inference, minimal age correction of $^{87}\text{Sr}/^{86}\text{Sr}$, or (ii) Sr remobilization, associated with a late-stage hydrothermal overprint by fluids carrying a radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signature, most likely sourced from regional lithologies (e.g., Andersen, 1984; Andrade et al., 1999; Hecht et al., 1999; Ackerman et al., 2015; Banerjee and Chakrabarti, 2019). While there is no direct relationship between Rb contents and $^{87}\text{Sr}/^{86}\text{Sr}$ (i), which would provide evidence for the ingrowth of radiogenic ^{87}Sr from Rb-rich compositions, the broadly positive correlation between $1/\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (i) (Supplementary Text 1) argues for selective leaching of primary magmatic Sr and its partial replacement by fluid-driven Sr with a distinctively radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signature. A similar process has been reported for Fen (Andersen, 1984, 1987), and a trend towards higher $^{87}\text{Sr}/^{86}\text{Sr}$ with decreasing Sr contents has also been observed for the Barra do Itapirapuã carbonatite in Brazil (Andrade et al., 1999) and Amba Dongar in India (Banerjee and Chakrabarti, 2019). The recrystallization of mineral phases carrying Sr is evident from the presence of secondary parisite (LREE-bearing fluorocarbonate) and thorite surrounded by Fe-chlorite in sample UC03, and apatite in sample UC02 from the Lemitar Mts. in which apatite cores are rich in Sr (up to ~10 wt.% SrO) while the altered rims are Sr-poor (~1 wt.% SrO) and calcite is devoid of Sr (Fig. 4c). Apatite frequently is affected by post-magmatic alteration (Bouzari et al., 2016; Horie et al., 2008). The alteration of apatite, filling of amygdales, and silicification thus appear to be the major processes modifying the Sr elemental and isotope systematics in the Lemitar Mts., whereas recrystallization of carbonate phases played a negligible role.

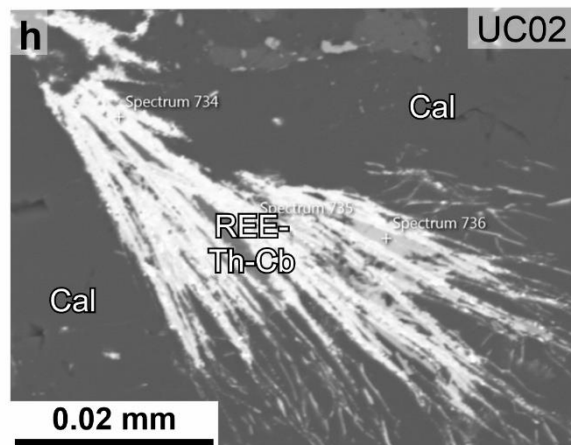
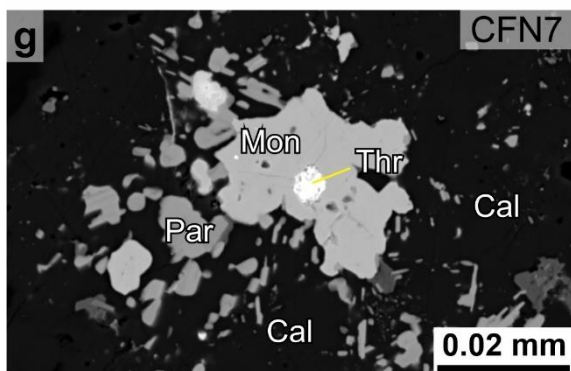
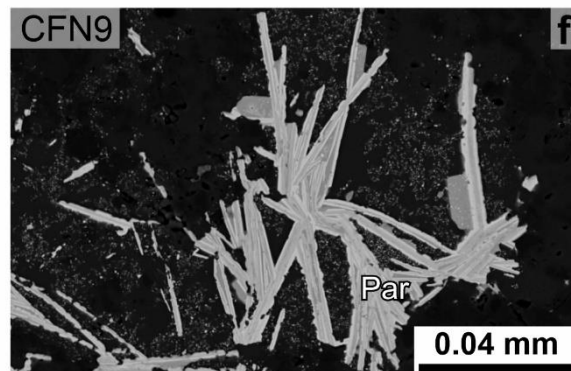
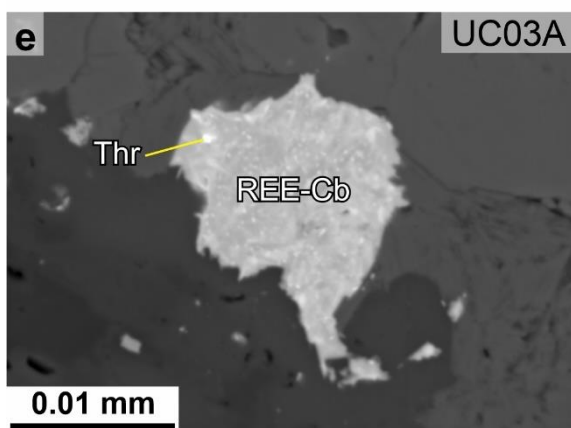
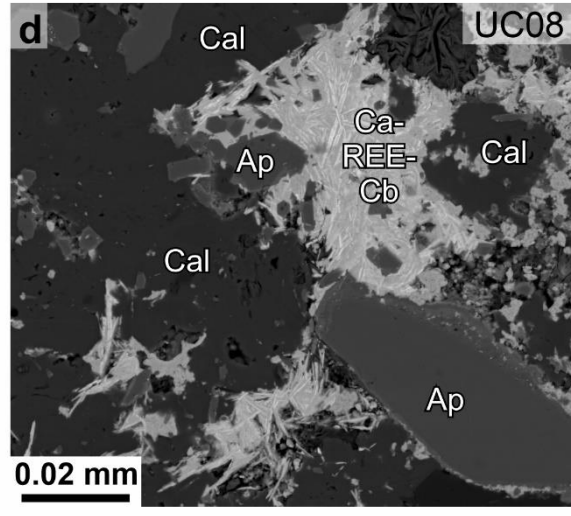
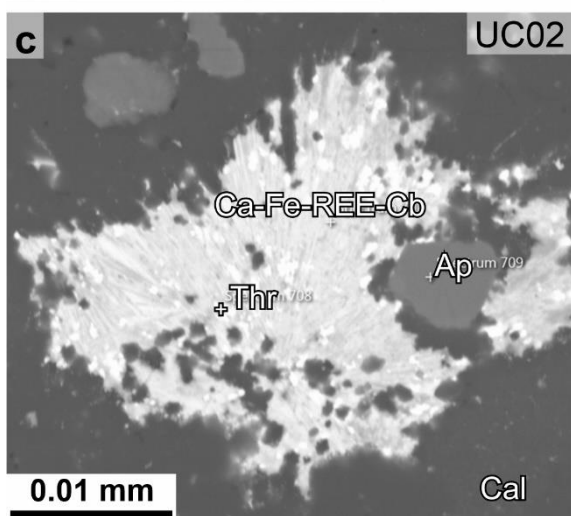
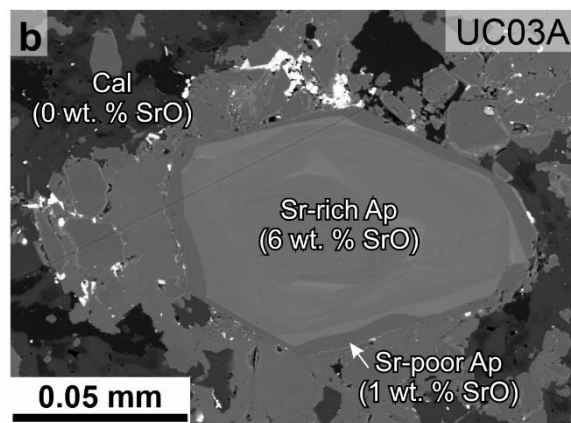
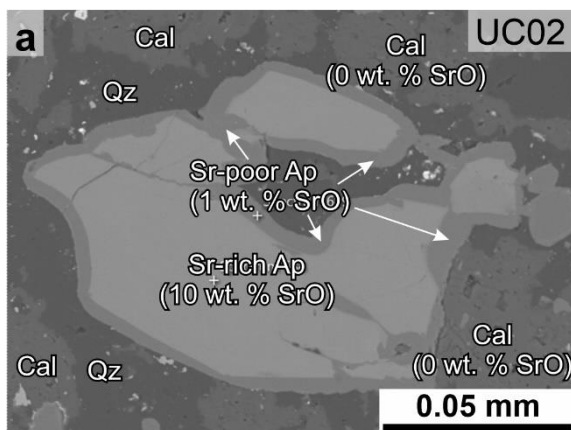


Fig. 2.4. BSE (back-scattered electron) images of features suggesting late- to post magmatic remobilization of Sr, REE, Th, U, and other elements in the Lemitar Mts. and Fen Complex carbonatites: a) Sr-poor rims of Sr-rich apatite (sample UC02, Lemitar Mts.); b) Sr-poor rims of Sr-rich apatite (sample UC03A, Lemitar Mts.); c) radial aggregates of thorite and Ca–Fe–REE-carbonate (sample UC02, Lemitar Mts.); d) aggregates of Ca–REE-carbonates (a mixture of several phases, sample UC08, Lemitar Mts.); e) aggregate of REE-carbonates enclosing thorite (sample UC03A, Lemitar Mts.); f) secondary paraisite in carbonatite CFN9, Fen Complex; g) monazite coating a small grain of thorite (sample CFN7); h) radial aggregate of secondary REE–Th-carbonate (sample UC02, Lemitar Mts.). Ap – apatite; Ca–Fe–REE–Cb – Ca–Fe–REE-carbonate; Cal – calcite; Ca–REE–Cb – Ca–REE-carbonate; Mon – monazite; Qz – quartz; Par – paraisite; REE–Cb – REE-carbonate; REE–Th–Cb – REE–Th-carbonate; Thr – thorite.

Hydrothermal alteration is further supported by the negative correlation between $^{87}\text{Sr}/^{86}\text{Sr}(\text{i})$ and $\delta^{18}\text{O}$ observed in the Lemitar Mts. carbonatites (note that two samples with $^{87}\text{Sr}/^{86}\text{Sr}$ close to ~ 0.704 reflect hydrothermal oxygen exchange; Supplementary Text 1). Vapor escape, for example in form of a surface-communicating hydrothermal system or degassing through volcanic crater, is a very effective process in oxygen isotope fractionation, as light oxygen escapes into vapor and residual water in the hydrothermal system becomes enriched in ^{18}O (e.g., Varekamp and Kreulen, 2000; Rapprich et al., 2024). Therefore, the interaction between carbonatites and hydrous fluids at elevated temperatures with the same origin would shift $\delta^{18}\text{O}$ towards higher values while it would not modify Sr isotope systematics because Sr contents of regional rocks, such as granites, likely are significantly lower than those of carbonatites. For Lemitar Mts. carbonatites, this process might be related to the re-activation of the Rio Grande Rift (McCalpin, 2005) during which $\text{F}+\text{H}_2\text{O}\pm\text{CO}_2$ -rich fluids reacted with the local Polvadera granite carrying highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}(\text{i})$ and low $\delta^{18}\text{O}$ values (Fig. S9). Consequently, hydrothermal alteration of carbonatites by these fluids would contribute between 16 and 30% to the Sr elemental and isotope signature of the Lemitar Mts. carbonatites indicated from the simple mixing model (more details in Ackerman et al., 2021 and Supplementary Text 1).

Collectively, the combined Sr–O isotope systematics should be considered with caution as they can be severely modified by late-stage alteration, recognized by the decoupled Sr–Nd systematics, highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$, and high $\delta^{18}\text{O}$. In contrast, late-stage alteration and possible REE mobilization appear to have a minimal effect on the Nd–C isotope systematics (see Andersen, 1987 for Nd) because no relationship between the degree of alteration (extent of recrystallization, degree of silicification), total REE contents (REE mobility) and Nd–C isotope compositions was recognized and the majority of global $\delta^{13}\text{C}$ carbonatite data resemble those of mantle-derived melts (Kyser, 1990).

2.4.2. The assessment of the global carbonatite database

The new Sr–Nd–C–O isotope data for samples from this study were complemented by a literature compilation of Sr–Nd–C–O isotope compositions for a total of 592 carbonatites from 101 occurrences in all geotectonic settings (Archean cratons, continental flood basalt regions, intraplate volcanic areas, ocean islands, rift zones, convergent margins) acquired from the GEOROC database (Sarbas and Nohl, 2008; accessed on October 2024, see Supplementary Text 2 and Tab S1 for the list of localities and geochemical data, respectively), and spanning the emplacement ages from the late Archean (~2.7 Ga) to recent (<2 Ma). Data from the database were filtered to remove the samples with apparent late-stage modification of Sr–Nd–C–O isotope systematics (e.g., highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and high $\delta^{18}\text{O} > 25\text{‰}$ at a given ϵ_{Nd}), or modification of parental silicate melts related to the assimilation of continental crust (e.g., Chandra et al., 2019; Yaxley et al., 2022) or even the assumed crustal origin of carbonate (e.g., Hegner et al., 2020; Su et al., 2024). Following this, we defined three principle groups of carbonatites although we note that there is some overlap in Sr–Nd isotope systematics among these groups (Fig. 2.2). We also emphasize that some samples do not strictly fit into these defined isotope boundaries due to late-stage metasomatism and/or alteration.

(1) **Group 1** carbonatites carry predominantly positive $\epsilon_{\text{Nd}}(\text{i})$ up to +6.6 and variable $\epsilon_{\text{Sr}}(\text{i})$ from ~−20 to +30 plotting on or close to the conventional “mantle array” in Sr–Nd isotope space. The most extensively studied carbonatite localities, e.g., the East African Rift System (e.g., Oldoinyo Lengai) or the North China Craton (e.g., Bayan Obo), plot within this group.

(2) **Group 2** carbonatites display a large variability in $\epsilon_{\text{Sr}}(\text{i})$ from ~+20 to +70 and slightly negative $\epsilon_{\text{Nd}}(\text{i})$ roughly between −10 and −1, plotting below the EM II end member composition and distinguishing them from **Group 1** carbonatites. Carbonatites from the Aldan Shield, Tarim Craton, Yangtze Craton, and Phalaborwa (Kaapvaal Craton) are the most notable occurrences. The origin of this group can be linked with a source that contains variable amounts of recycled marine carbonates delivered to the mantle via subduction whereby marine carbonates are considered to be the dominant source of recycled carbon (Fig. 2.5b). Indeed, sub-continental lithospheric mantle fluxed with CO_2 -rich melts/fluids derived from subducted, carbonate-rich marine sediments characterized by high $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Fig. 2.3), has been suggested as a source of carbonatites in the Yangtze Craton (Dalucão, Maonuiping, Lizhuang; Hou et al., 2015), and other localities such as Naantali in Finland (Li et al., 2018; Woodard and Huhma, 2015; Xu et al., 2018). Besides, the incorporation of recycled marine sediments was suggested for several carbonatite occurrences on the basis of Ca and/or S isotope compositions (Amsellem et al., 2020; Banerjee et al., 2021; Bolhar et al., 2020) although Sun et al., (2021) concluded that carbonatites from their study (e.g., Oka, Belaya Zima, Songwe Hill, Kovdor, among others) might have accommodated <2% recycled Phanerozoic carbonates. In contrast,

Hulett et al., (2016) posited that worldwide carbonatites younger than ~300 Ma carry a significant imprint of recycled crust, based on the elevated $\delta^{11}\text{B}$ values, which has also been corroborated more recently for carbonatites from British Columbia (Çimen et al., 2019).

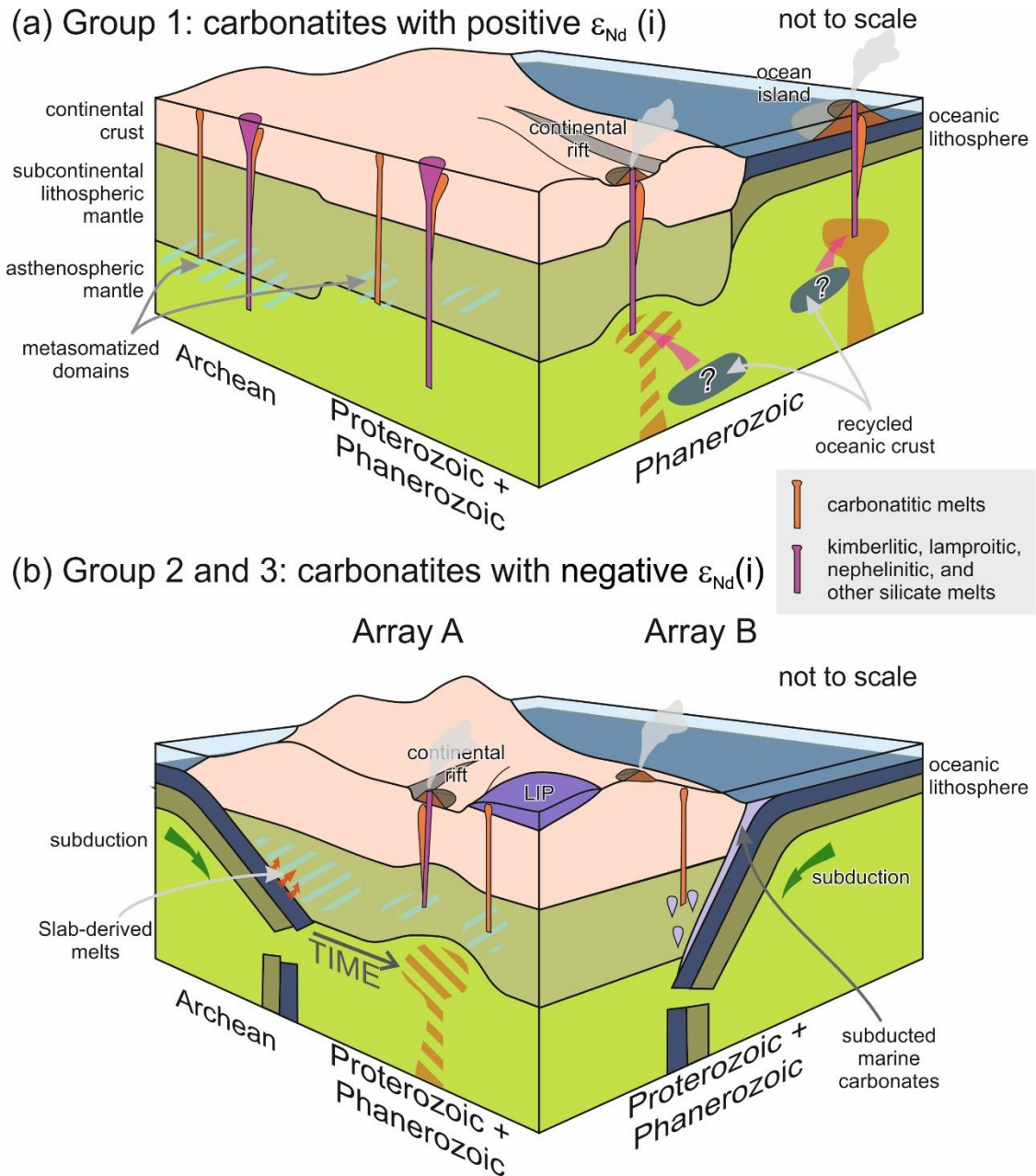


Fig 2.5. An illustrative cartoon depicting the sources and petrogenesis of global carbonatites worldwide with respect to the observed Sr–Nd–C–O isotopic signatures (see the text for details).

(3) **Group 3** carbonatites show variable, broadly “crustal-like” Sr–Nd isotope compositions (i.e., negative $\epsilon_{\text{Nd}}(\text{i})$ down to -18.3 and $\epsilon_{\text{Sr}}(\text{i})$ up to $\sim +90$ Fig. 2.2, Tab S1). This group is characteristic of carbonatite bodies from intraplate settings (e.g., Tarim (Matcha, Taohuala), Tamil Nadu, Paraná–

Etendeka LIP). We explore the possible explanations for the formation of this latter group in Section 4.4.

2.4.3. The longevity of a depleted mantle source parental to carbonatite magmas

The long record of carbonatite occurrences since the Archean implies that the processes that generate carbonatite melts (Bell and Blenkinsop, 1989; Tilton and Bell, 1994) must have been operational for at least as long as the modern style of plate tectonics >3 Ga (Bell and Simonetti, 2010; Gamal El Dien et al., 2020). The similar Sr–Nd–C–O isotope compositions of **Group 1** carbonatites found in Archean cratons and Proterozoic–Phanerozoic continental crust indicates derivation of these carbonatites from a volatile-rich mantle source. Because the majority of **Group 1** carbonatites display mantle-like $\delta^{13}\text{C}$ signatures (Fig. 2.3), the volatiles were either added through metasomatism by transient, mantle-derived CO_2 -rich melts/fluids or delivered from the deep Earth by mantle plumes (e.g., Yaxley et al., 2019; Fig. 2.5a). The compilation of Sr–Nd–C–O isotope data on global carbonatites reveals that at least until the late Proterozoic, the **Group 1** carbonatites were derived from a mantle source which must have been depleted relative to a chondritic Earth with high positive $\epsilon_{\text{Nd}}(i)$ (Figs. 2.6 and 2.7). Importantly, a regression through the **Group 1** carbonatite data overlaps with that found for global kimberlites which are assumed to reflect the 2.5 Ga long evolution of a deep and isolated mantle reservoir (Woodhead et al., 2019) although Giuliani et al. (2021) estimated the time of formation of the kimberlite source to >3.5 Ga and possibly older, approaching the age of Earth's accretion. The necessity of a long-term isolated mantle reservoir is in contrast with the conclusions given by (Tappe et al., 2020a) questioning the model of the derivation of >200 Ma kimberlites from such an isolated reservoir on the basis of the combined $^{182}\text{W}/^{184}\text{W}$ and Hf–Nd isotope data from multiple occurrences of kimberlites from Africa. We note that the majority of kimberlites with Hf–Nd isotope compositions plotting along the terrestrial array (Chauvel et al., 2008) are positioned in the Kaapvaal craton and wider area of the African large low shear-wave velocity province (Tappe et al., 2020a, 2020b), which, however, does not alleviate the need for a more global isolated deep mantle reservoir that would be disseminated in other regions as well. In fact, a more recent stable W isotope survey of kimberlites from several other worldwide kimberlite occurrences provides permissive evidence for such an early formed and long-lived mantle reservoir (Nakanishi et al., 2021).

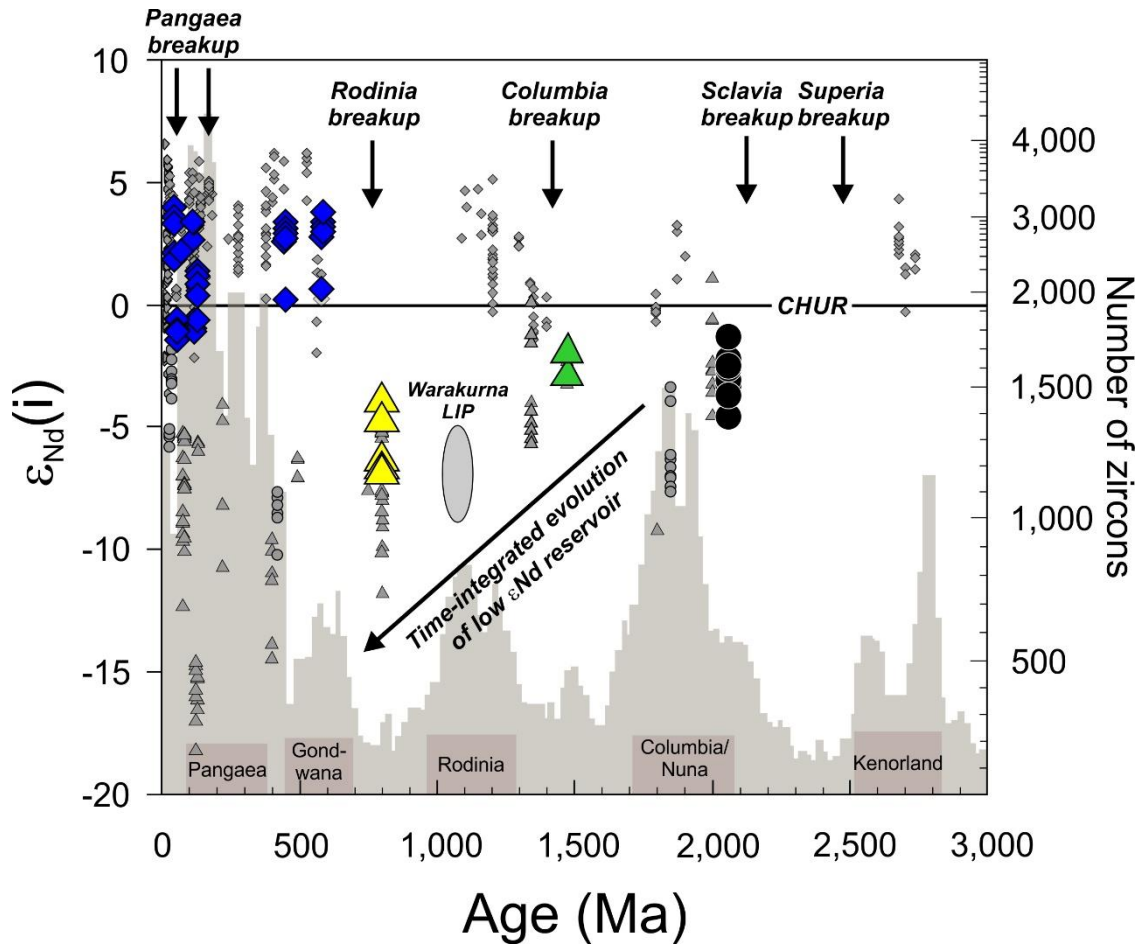


Fig. 2.6. Occurrences of carbonatites worldwide in the last 3 Ga and their $\epsilon_{\text{Nd}}(i)$ signatures along with the histogram of U–Pb zircon ages. It can be recognized that the global distribution of carbonatites belonging to proposed groups appears to be correlated with major crustal events which are thought to be related to the formation of super-continents. Symbols are the same as in Fig. 2.2. Bigger symbols are samples analyzed in this study. Zircon populations were redrawn from Hawkesworth et al., 2020.

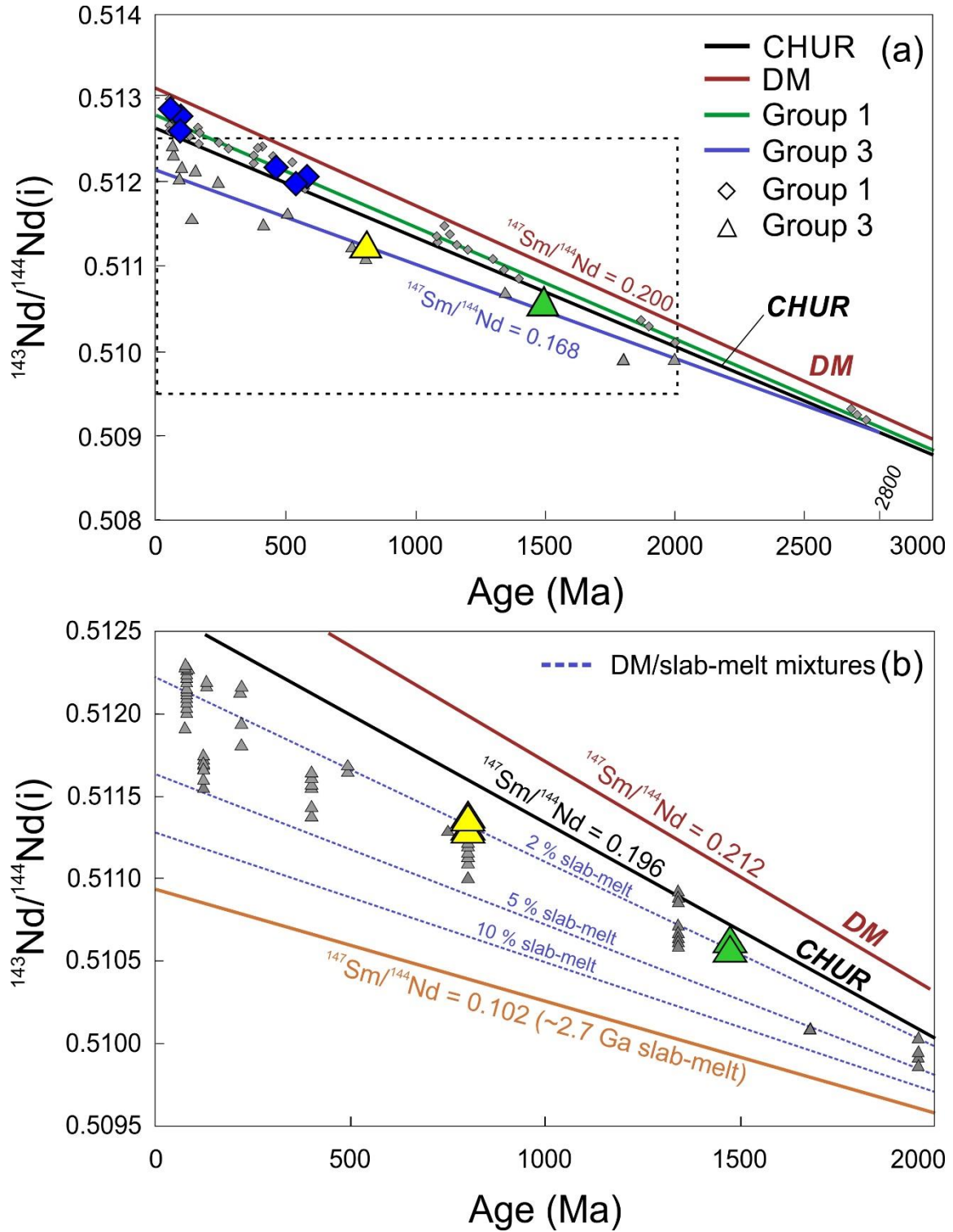


Fig. 2.7. Neodymium isotopic ($^{143}\text{Nd}/^{144}\text{Nd}$) evolution of global carbonatites belonging to proposed groups (**Group 1** and **Group 3** with positive and negative ϵ_{Nd} signatures, respectively) and selected reservoirs (DM, CHUR) from ~3.0 Ga to present (adopted from Woodhead et al., 2019). (a) the composition of **Group 1** carbonatites indicates derivation from a single long-lived reservoir that was depleted compared to CHUR. On the other hand, lower median $^{143}\text{Nd}/^{144}\text{Nd}$ signatures with respect to CHUR at a given time found in the **Group 3** carbonatites require the addition of ancient low Sm/Nd material into their mantle sources. (b) more detailed inset from ~2.0 Ga showing that the composition of the **Group 3** carbonatites can be best explained by the 2–10% incorporation of ~2.7 Ga slab-derived melt to their mantle sources. See the text for more details and Tab 3 and Tab S3 for the end-members used in the calculations. Bigger symbols are samples analyzed in this study.

Table 2.3: Mixing parameters used for modeling average values of Group 1

	Sr (ppm)	Nd (ppm)	$\epsilon_{\text{Sr}}(\text{i})$	$\epsilon_{\text{Nd}}(\text{i})$
Mantle end member	94 ^a	5 ^a	-10 ^a	3.6 ^a
Marine carbonate	400 ^b	40 ^b	63.9 ^b	-8.5 ^b
Taohuala carbonate sediment				-12 ^d

^a Sarbas and Nohl, 2008; ^b Faure, 1987; ^c Li et al., 2018; ^d Xue et al., 2018

Tab. 2.3 Mixing parameters used for modeling average values of Group 1

Compared to kimberlites, Phanerozoic carbonatites derived from this putative common mantle reservoir do not systematically deviate towards lower but still radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ ratios at <200 Ma (cf. Woodhead et al., 2019). Rather, the <200 Ma **Group 1** carbonatites show a general, albeit slightly scattered distribution along the regression line that can be best explained by their derivation from sub-lithospheric depleted mantle mixed with variable proportions of enriched mantle reservoirs (e.g., EM I; Bell and Simonetti, 2010) but derivation from a geochemically less depleted component (FOZO–PREMA; focal zone–prevalent mantle) mixed with EM I could also result in such Sr–Nd isotope signatures, as advocated for kimberlites (Giuliani et al., 2021), because there have so far been no carbonatites identified which would extend towards the most depleted DM-like compositions (Yaxley et al., 2022). Strongly depleted compositions beyond FOZO–PREMA towards DM sensu stricto are unlikely to produce carbonate-rich liquids because their geochemically depleted character, including incompatible elements, largely precludes formation of volatile-rich reservoirs (e.g., Sanfilippo et al., 2022).

2.4.4. Significance of unradiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ signatures in carbonatites: Evidence for a long-lived enriched mantle reservoir?

The formation of carbonatites is still a matter of debate but there is an increasing body of evidence attesting to their non-primary mantle origin (e.g., Lee and Wyllie, 1998; Weidendorfer et al., 2016; Yaxley et al., 2022). About one-third of worldwide carbonatites (**Group 2** and **Group 3**) display negative $\epsilon_{\text{Nd}}(\text{i})$ and predominantly positive $\epsilon_{\text{Sr}}(\text{i})$ values (Fig. 2.2), plotting away from conventional mantle end members irrespective of their distinctively different emplacement ages and geotectonic position. The coupled Sr–Nd isotope compositions of these carbonatites carrying unradiogenic Nd isotope signatures with $\epsilon_{\text{Nd}}(\text{i})$ as low as -18.3 (Fig. 2.2) argue for distinct sources, formed either

through the addition of enriched materials, such as marine sediments or recycled crust, or metasomatism by yet unconstrained agents in the source mantle. For the latter, cratonic lamproites and similar mantle-derived alkaline magmas can also carry a notably depleted Nd isotope signature (e.g., Smith, 1983; Fraser et al., 1985; Nelson, 1989; Nowell et al., 2004; Becker and Roex, 2006) although these compositions may be less common while carbonatites with similarly enriched Sr–Nd isotope systematics are more frequent (Yaxley et al., 2022 and this study).

In particular, the **Group 3** carbonatites are typified by steeply decreasing $\epsilon_{\text{Nd}}(i)$ values as low as -18.3 that pass through the putative EM I mantle end member at rather variable $\epsilon_{\text{Sr}}(i)$ (-10 to <80), clearly distinguishing them from both **Group 1** and **Group 2** carbonatites and necessitating other types of enriched compositions than conventional mantle members. The **Group 3** carbonatites predominantly occur in, or in close association with, cratons and their collision zones (Paraná–Etendeka LIP, Sao Francisco Craton, Spitskop in Kaapvaal Craton, Tarim–North China Craton in Luliangshan region, Tamil Nadu in India, Sri Lanka, central and east China; Ye et al., 2013; Ackerman et al., 2017; Guarino et al., 2017; Vrublevskii et al., 2018). The $^{143}\text{Nd}/^{144}\text{Nd}$ evolution of the **Group 3** carbonatites reveals that they plot along a single path with a distinctly steeper $\epsilon_{\text{Sr}}(i)$ – $\epsilon_{\text{Nd}}(i)$ slope (and with distinctly lower Sm/Nd ratios) compared to primitive (CHUR) and depleted mantle evolution curves (FOZO–PREMA, DM; Fig. 2.7). Interestingly, the regression of the median $^{143}\text{Nd}/^{144}\text{Nd}$ values for **Group 3** carbonatites ($r^2 = 0.94$) intersects the CHUR evolution curve at ~ 2.8 Ga (Fig. 2.7), which is similar to the modelled time of isolation of the mantle source of global kimberlites at ~ 2.5 Ga (Woodhead et al., 2019); note that Giuliani et al. (2021) have recently estimated the time of formation of the kimberlite source at even older age of >3.5 Ga. While these estimated ages for the formation of carbonatites and alkaline silicate melts are somewhat different, this does not preclude the formation of carbonatite magmas at more ancient periods, exemplified by ~ 3 Ga Tupertalik carbonatite (Bizzarro et al., 2002). The calculated present-day $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of ~ 0.51214 with $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of ~ 0.168 for **Group 3** carbonatites is much lower than the present-day $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of ~ 0.51264 and $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of ~ 0.197 observed for **Group 1** carbonatites presumably derived from the depleted upper mantle or through liquid immiscibility/by extreme magmatic fractionation from the depleted mantle-derived melts. Moreover, the consistently unradiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ values for **Group 3** carbonatites, which span a range in emplacement ages (76 Ma to 2 Ga) indicate derivation from a long-lived and isolated enriched mantle source that has evolved at least from the late Archean (<2.8 Ga) and perhaps even older. Otherwise, these carbonatites would be incapable of arriving at such unradiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ compositions due to mixing with high-Sm/Nd components. In fact, the existence of convectively isolated reservoirs throughout the Earth’s history has been evidenced on the basis of ^{182}W and $^3\text{He}/^4\text{He}$ isotope systematics (e.g., Mundl–Petermeier et al., 2019; Tusch et al., 2021). This may appear to be in conflict with, for example, the necessity for short-term pre-eruptive storage of carbonatites assessed from the Lu–Hf isotope

systematics of selected carbonatites from South Africa, East African rift, and Canadian Shield (Bizimis et al., 2003). We note that Lu/Hf elemental ratios in carbonatites often are $> \sim 100$, leading to a rapid evolution of radiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ ratios even within a geologically short timescale. In contrast, Sm/Nd ratios in carbonatites commonly are much lower ($\sim 0.1\text{--}0.2$) which does not allow for the forming of a particularly ^{143}Nd -enriched signature even after a protracted period of time.

Several plausible explanations can be considered for the formation of **Group 3** carbonatites:

(i) Most carbonatite occurrences in the **Group 3** are closely connected with old cratons predominantly built by the Archean crust carrying $\epsilon_{\text{Nd}}(\text{i})$ signature that may have evolved towards present-day negative values. Contribution from the lower continental crust appears less plausible because of its either high Sm/Nd ratio (0.143–0.224; Dai et al., 2008) and consequently positive $\epsilon_{\text{Nd}}(\text{i})$, or typically significantly positive $\epsilon_{\text{Sr}}(\text{i})$ values (Othman et al., 1984) due to its high-Rb/Sr nature. Similarly, contamination of parental carbonated silicate melts by the Archean–Paleoproterozoic continental crust (King, 2005) present at the **Group 3** carbonatite sites during their ascent to the surface cannot explain the steep character of the array (low Rb/Sr in comparison to the wide range but typically high Rb/Sr recorded in the Archean crust; (e.g., Martin and Moyen, 2002 and references therein). In particular, all **Group 3** carbonatites display a broadly similar slope in the Sr–Nd isotope space (Fig. 2.2), irrespective of the range of their emplacement ages from ~ 2 Ga to 76 Ma as well as distinctive geographic/geotectonic positions. Moreover, there is an apparent trend towards progressively more negative $\epsilon_{\text{Nd}}(\text{i})$ values with a younger emplacement age of **Group 3** carbonatites (Figs. 2.6 and 2.7) indicating derivation from a broadly similar long-lived source to be capable to evolve toward such a negative ϵ_{Nd} composition. While many carbonatites likely originated through liquid immiscibility from alkaline silicate magmas and Sr isotope systematics can suffer from post-emplacement modifications (see Section 4.1), the comparably negative $\epsilon_{\text{Nd}}(\text{i})$ values observed for **Group 3** carbonatites and coeval associated alkaline silicate rocks (e.g., Tamil Nadu – Ackerman et al., 2017; Paraná–Etendeka LIP – Speziale et al., 2020 and references therein) argue for similar, if not identical, sources of these carbonatites and spatially related silicate rocks (Table S2). Moreover, if the negative $\epsilon_{\text{Nd}}(\text{i})$ values were a result of crustal contamination, then the Nd abundances would be directly dependent on/linked with SiO_2 contents, a feature which is observed neither in carbonatites nor in associated alkaline rocks (not shown; Tab S2). Thus, large variations in $\epsilon_{\text{Nd}}(\text{i})$ (Fig. 2.6) and $^{143}\text{Nd}/^{144}\text{Nd}(\text{i})$ (Fig. 2.7) reflect different proportions of low-Sm/Nd material delivered to a mantle source (see below) rather than different amounts of crustal material directly incorporated into carbonatite melts.

(ii) Kimberlites, lamproites, lamprophyres, and similar potassic mantle-derived melts often are genetically associated with carbonatites (e.g., Tappe et al., 2008; Ernst, 2014) and it has been suggested that carbonatite magmas may form as exsolution products of deep-originated kimberlitic/lamprophyric magmas *en route* to surface (Tappe et al., 2017). However, metasomatism of a common mantle reservoir by LREE-enriched mantle-derived melts of above mentioned rocks can be ruled out for at least two reasons. First, many of these rocks that show $\epsilon_{\text{Nd}}(\text{i}) < 0$ are Phanerozoic in age and, therefore, considering their highly variable $\epsilon_{\text{Nd}}(\text{i})$ values that are related to local metasomatism (e.g., those found in lamproites; Krmíček et al., 2016), they are unable to represent a single and uniformly evolved global reservoir since the Archean. Second, the Precambrian kimberlites show overall radiogenic ($\epsilon_{\text{Nd}}(\text{i}) > 0$) signatures (Woodhead et al., 2019 and references therein) although, at the same time, some of these kimberlites tend to have negative ϵ_{Hf} values (e.g., Tappe et al., 2020b; Tappe et al., 2020a). We note, however, that such Nd–Hf isotope systematics are not uniform because wide ranges in ϵ_{Hf} from positive to negative values have been reported for kimberlites and/or ultramafic lamprophyres even from a single locality (e.g., Eastern Dharwar, Eastern Goldfields-Norseman, Kuruman; see Giuliani et al., 2021).

(iii) Ancient (Archean) metasomatism of the source mantle of the **Group 3** carbonatites by carbonate-rich melts carrying low Sm/Nd and Rb/Sr ratios (Ray et al., 2013) would ultimately lead to the required steep slope of the **Group 3**, or even a combined ϵ_{Sr} and ϵ_{Nd} negative signatures (e.g., Newania, Fig. 2.2, Supplementary Text 1). However, the extent of carbonate-rich metasomatism in the Archean is unknown and given the rare occurrences of Archean carbonatites and associated silicate compositions, metasomatism of the source mantle by carbonate-rich melts remains questionable. The overall low amount of Archean carbonatites may, in part, be caused by limited volumes of the Archean crust preserved due to recycling as well as by pronounced vulnerability of carbonates in a thinned crust/rift to subsequent reworking in convergent margins. Besides, Woolley (1989a) described rare extrusions of ancient carbonatites while the frequency of carbonatite occurrences increased with time (Fig. 2.6). Whether this may be related to an increased volume of carbonates incorporated into the mantle with time (Cameron and Baumann, 1971; Veizer et al., 1989), is unclear at present but it could be a viable alternative.

(iv) Melting of an enriched (low-Sm/Nd) mantle reservoir (Kumar et al., 1998) either metasomatized by slab-derived melts during the Archean (Davies and Bunge, 2006) or containing large proportions of delaminated Archean continental crust (Woodard and Huhma, 2015) could also account for these unradiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ signatures. Evidence for common late Archean interaction (metasomatism) between LREE-enriched slab-derived melts and mantle is well-documented by the occurrence of Mg–K-rich sanukitoids (high-Mg granitoids), a lithology that originated between ~2.9

and 2.5 Ga and is characteristic of all late Archean terranes (e.g., Halla, 2005; Martin et al., 2005; Laurent et al., 2014 and references therein). Indeed, a direct relationship between sanukitoid-like melts and carbonatites has been invoked in West Greenland based on their close spatial relationship and similar trace element distributions (Steenfelt et al., 2005). Also, a ~2.94 Ga metasomatic assemblage formed between trondhjemite intrusive into dunite was found (Whyatt et al., 2020), indicating the existence of silicic fluids at elevated $T > 600^{\circ}\text{C}$, as well as Archean siliceous metasomatism of the Kimberley area (Bell et al., 2005). Although the sources of such metasomatism are debated, there is ample evidence for Archean subduction zone-derived melts interacting with the mantle (Antonelli et al., 2021; Bell et al., 2005; Whyatt et al., 2020), and contamination of the mantle by recycling of nitrogen-rich Archean sediments has also been indicated (Smart et al., 2016).

In order to constrain the possible amount of Archean slab-derived melts that need to be delivered into and mixed with convective mantle for explaining the $^{143}\text{Nd}/^{144}\text{Nd}$ composition of the **Group 3** carbonatites, we applied a two-stage model similar to that used for kimberlites by Woodhead et al. (2019). First, $^{143}\text{Nd}/^{144}\text{Nd}$ isotope evolution of the average ~2.7 Ga slab-melt was evaluated (Fig. 2.7) using the present-day Sm–Nd elemental and isotope systematics of ~2.8–2.7 Ga slab melts represented by the average of global TTG-melts (*sensu stricto*; Moyen and Martin, 2012), and sanukitoids. Then, mixing of such a slab-derived melt from ~2.7 Ga at different proportions with either primitive (CHUR-like) or depleted mantle (DM), the latter representative of a mantle source of many **Group 1** carbonatites, produces mixing arrays with $^{143}\text{Nd}/^{144}\text{Nd}$ slopes corresponding to different parent/daughter ratios of the mixtures. Using this approach, we find that the observed $^{143}\text{Nd}/^{144}\text{Nd}$ evolution of the **Group 3** carbonatites can be successfully reproduced by mixing the DM source mantle with 2–10% of ~2.7 Ga slab melt, represented by those TTG (Fig. 2.7). We note that such an amount of siliceous slab-derived melt added to the mantle source would result in the addition of less than ~6 wt. % SiO_2 which is not at odds with a silica-deficient character of direct low partial melting degree carbonatites and/or typical carbonate-rich silicate melts from which carbonatite melts are further exsolved through the liquid immiscibility. We thus envision a scenario in which **Group 3** carbonatites originated either directly or through liquid immiscibility from alkaline silicate melts during their ascent, both derived from sub-lithospheric mantle possibly metasomatized by slab-derived melts in the Archean, aided by the accumulation of volatiles to form a reservoir capable of producing carbonatite melts (Fig. 5b).

2.5. Are there links between carbonatites and life cycles of super-continents?

On Earth, subduction has likely operated since at least 3 Ga (Gamal El Dien et al., 2020; Sobolev et al., 2019), and continental crust became progressively thicker at <3 Ga (Dhuime et al., 2015), consistent with other lines of evidence for establishing isotopically distinguished reservoirs early in the Earth's history (Porcelli and Elliott, 2008). Carbonatites with unradiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ (i.e., negative ϵ_{Nd}) compositions started to emerge in greater numbers in the Paleoproterozoic (Fig. 2.6), underscoring the necessity for isotopically evolved materials to exist long before because vigorous mantle convection and mixing of subducted materials were probably enabled only following the formation and stabilization of cratons some 500–700 Myr after non-plate tectonics mode ceased (Cawood et al., 2018).

The worldwide occurrences of carbonatites appear to show a broad spatial and temporal relationship to the formation and/or breakup of super-continents (Kenorland, Columbia/Nuna, Rodinia, Gondwana/Pangea; Burke et al., 2003) because carbonatites appear to be closely tied in time and space to these major crust formation events (72% of carbonatites are formed during within these events). The maxima in the distribution of zircon populations (Hawkesworth et al., 2020) can be related to the super-continent assembly (enhanced formation of the crust through ocean–continent, and continent–continent collisions) whereas the minima can be linked with the continental breakup (Bradley, 2011; Fig. 2.6). The formation of late Archean Kenorland remains puzzling (Bleeker, 2003) but carbonatites with positive $\epsilon_{\text{Nd}}(\text{i})$ (Superior Province, Karelia) appear to be linked with extensive magmatic activity leading to the assembly of Superia at ~2.7 Ga. Paleo–Mesoproterozoic super-continent of Columbia/Nuna was amalgamated from several crustal blocks (Zhao et al., 2004) and the prevalence of carbonatites with negative $\epsilon_{\text{Nd}}(\text{i})$ values and largely positive $\epsilon_{\text{Sr}}(\text{i})$ (**Group 2**) may indicate variable involvement of carbonate-rich marine sediments (Xie et al., 2019) during the Columbia/Nuna formation. The prolonged breakup of Columbia/Nuna at ~1.6–1.2 Ga caused by extensive rifting due to a mantle plume and/or mantle upwelling (Zhao et al., 2004) is associated with the occurrence of ~1.4–1.3 Ga carbonatites, predominantly derived from the ancient enriched mantle reservoir (**Group 3** carbonatites). The breakup of Rodinia associated with widespread continental rifting (825–740 Ma) due to the formation of a super-plume (Li et al., 2008) is marked by ~800 Ma Tamil Nadu and Tarim carbonatites with pronounced negative $\epsilon_{\text{Nd}}(\text{i})$ signatures (Fig. 2.2). Formation of Gondwana and Pangea during the Neoproterozoic–Phanerozoic is associated with widespread silicate alkaline and carbonatite magmatism related to large-scale continental rifting (e.g., East African Rift), continental flood basalt/LIP provinces, convergent margins, and OIB settings (Fig. 2.6). Many of these LIPs (e.g., Paraná–Etendeka) are directly related to the prolonged breakup of Pangea between ~175 and 55 Ma (Veevers and Tewari, 1995). The extreme range of $\epsilon_{\text{Nd}}(\text{i})$ values from +7 down to –17 is indicative of heterogeneous mantle sources of carbonatite magmas during this period, suggesting the extended

chemical and isotope heterogeneity of all reservoirs included in the formation of carbonatite melts with time possibly related to large-scale source mantle metasomatism (see also Woodhead et al., 2019).

2.6. Conclusions

By examining more than 590 worldwide carbonatites for their coupled Sr–Nd isotope systematics, three main groups are distinguished. The source of **Group 1** carbonatites, characterized by positive $\epsilon_{\text{Nd}}(\text{i})$, is identified in the depleted mantle rich in volatiles. This group of carbonatites became slightly isotopically more heterogeneous in the late Proterozoic as a consequence of a larger amount of subducted material incorporated into the mantle. **Group 2** displays variable but predominantly negative $\epsilon_{\text{Nd}}(\text{i})$ and radiogenic $\epsilon_{\text{Sr}}(\text{i})$. Whereas **Group 2** carbonatites composition appears to reflect variable amounts of marine sediments including carbonates assimilated into the mantle source, the composition of the **Group 3** carbonatites can be best explained by a derivation of parental melts from a sub-lithospheric mantle source metasomatized by 2–6% slab-derived melts with low Sm/Nd being largely isolated since the late Archean (~2.7 Ga) in order to produce negative $\epsilon_{\text{Nd}}(\text{i})$ as low as –18.3. Combined with distinctly different emplacement ages of **Group 3** carbonatites, this would require a long-term isolation of such a source because the regression line intersects with a chondritic uniform reservoir at ~2.7–2.8 Ga. We also posit that global carbonatite occurrences are broadly linked with the life cycles of super-continent. It may well be that future detailed scrutiny of data for carbonatites, kimberlites, and LIPs may reveal close mutual inter-relations.

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Chapter 3:

Highly siderophile element geochemistry and Re–Os isotopic systematics of carbonatites: Insights from Tamil Nadu, India

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Abstract

Carbonatite metasomatism has been widely implicated for worldwide mafic mantle suites but so far, no combined data have been available for highly siderophile element systematics (HSE – Os, Ir, Ru, Pt, Pd, Re) and Re–Os isotopic compositions in carbonatites themselves. We present the first systematic survey of the HSE and Re–Os isotopic compositions in a suite of well-characterized Neoproterozoic carbonatites, silicocarbonatites and associated silicate rocks (pyroxenites, monzogabbros, syenites) from south India in order to place constraints on the HSE systematics in carbonatite magmas, anchoring possible mantle sources of carbonatites and relationship to the ambient crustal lithologies as well as preliminary constraints on carbonatite metasomatism in Earth's mantle. The most plausible explanation for generally low HSE contents in calciocarbonatites from Tamil Nadu (HSE <1.22 ppb) involves a low-degree (<1%) partial melting of the mantle source producing sulfur-saturated carbonatitic magmas leaving behind sulfide phases retaining HSE. The new data also indicate a strong FeO control on the distribution of Os and Pt during segregation of carbonatite melt from its enriched mantle source and/or melt differentiation. The combined ¹⁸⁷Re/¹⁸⁸Os values (from 0.10 to 217), ¹⁸⁷Os/¹⁸⁸Os ratios (0.186–10.4), and initial γ_{Os} values back-calculated to 800 Ma (from +0.1 to +6052) predict that most Tamil Nadu calciocarbonatites were plausibly derived from a

carbonated peridotite source with <10% recycled component. This model would thus provide significant constraints on the origin/source of carbonatites, irrespective of their post-emplacement history. The unusual, volumetrically rare, Mg–Cr-rich silicocarbonatites ($\Sigma\text{HSE} = 14\text{--}41$ ppb) display almost identical HSE patterns with those of host pyroxenites and predominantly high Pt (up to 38 ppb), the origin of which remains unknown. Positive co-variations between Pt, Pd, and Re, and the well-developed positive correlation between Pt and MgO in these Mg–Cr-rich silicocarbonatites argue for a source coming predominantly from the upper mantle. The Re–Os isotopic systematics agree with direct incorporation of enriched mantle-derived material into parental melts but variable incorporation of potassium-rich crustal materials is evidenced by highly positive γ_{Os} 800Ma values for a sub-suite of Mg–Cr-rich silicocarbonatites, indicating intense fenitization. The highly radiogenic Os isotopic compositions of monzogabbros and a syenite argue for their derivation from crustal lithologies with no or only negligible contribution of mantle material. Collectively, low Ir, Ru, Pt, and Pd contents found in the Tamil Nadu carbonatites appear to indicate the incapability to significantly modify the total budget of these elements in the Earth's mantle during carbonatite metasomatism. In contrast, very high Re/Os ratios found in some of the analyzed carbonatites, paralleled by extremely radiogenic $^{187}\text{Os}/^{188}\text{Os}$ signature, can produce large modification of the Re–Os isotopic composition of mantle peridotites during carbonatite melt percolation when high melt/rock ratios are achieved.

Keywords: HSE, Re–Os isotopic systematics, carbonatite, silicate, enriched mantle, metasomatism

3.1. Introduction

Mantle-derived magmas can potentially provide direct information about the composition and nature of their mantle sources. However, this is highly dependent on their vulnerability to modification *en route* to surface through processes of fractional crystallization and/or crustal assimilation fractional crystallization and interaction with the lithospheric mantle at depth which may modify the original inventory extensively. Mantle-derived carbonatite melts represent an exceptional type of magma due to their peculiar physical properties such as extremely low viscosity and liquidus temperatures as low as 600 °C (Jones et al., 2013 and references therein), which enable expeditious transport from the Earth's up-per mantle to shallow levels and rapid impregnation of mantle lithologies (Hammouda and Laporte, 2000). In addition, carbonatite magmas are thought to represent an efficient agent for large-scale metasomatism, producing light rare earth element (LREE) enrichments, paralleled by high field-strength element (HFSE) depletions and vast changes in the mineralogy (e.g., olivine and/or clinopyroxene precipitation), documented on worldwide subcontinental lithospheric mantle xenolith suites (e.g., Ackerman et al., 2013b; Coltorti et al., 1999; Ionov et al., 1993; Rudnick et al., 1993; Yaxley et al., 1991). Carbonatitic magmas are also thought to be responsible for the electric conductivity anomalies observed near the asthenosphere–lithosphere boundary (Gaillard et al., 2008) and mid-lithospheric discontinuities interpreted as a result of crystallization of seismically slow minerals including carbonates (Rader et al., 2015).

Three different processes are usually considered to be responsible for the formation of carbonatite magmas: (1) liquid immiscibility of carbonatite and silicate melts (e.g., Brooker and Kjarsgaard, 2011; Freestone and Hamilton, 1980; Koster van Groos and Wyllie, 1966), (2) fractional crystallization of a carbonate-rich alkaline silicate magma (e.g., Lee and Wyllie, 1994; Watkinson and Wyllie, 1971), and (3) partial melting of carbonate-bearing mantle peridotite or eclogite (e.g., Dalton and Presnall, 1998; Dasgupta et al., 2013; Ghosh et al., 2009; Wallace and Green, 1988). During the melting of CO₂-bearing mantle lithologies, only minute fractions of carbonatite melt (<0.3%; Dasgupta and Hirschmann, 2006) form rapidly evolving to carbonated silicate melts with higher fraction (e.g., Dasgupta et al., 2013; Gudfinnsson and Presnall, 2005), and the stability of these melts largely depends on several parameters such as pressure, temperature, oxygen fugacity and/or H₂O content (Dasgupta, 2018; Dasgupta et al., 2013; Ghosh et al., 2014; Gudfinnsson and Presnall, 2005).

Highly siderophile element (HSE – Os, Ir, Ru, Pt, Pd, Re) geochemistry, combined with Re – Os isotopic determination, has proven to represent a unique and powerful tool for tracing formation and evolution of mantle-derived rocks such as mid-ocean ridge basalts (MORB – Bézoz et al., 2005; Gannoun et al., 2016; Rehkämper et al., 1999), ocean-island basalts (OIB – Day, 2013; Day et al., 2010), intra-plate alkaline basalts (Day et al., 2013; Gannoun et al., 2016; Rocha-Júnior et al., 2012), and komatiites (Puchtel and Humayun, 2005). This is due to strong partitioning of HSE into sulfides

and metallic phase over co-existing silicates during melting and fractional crystallization (Brenan et al., 2016 and references therein) and fractionation of bulk HSE during mantle melting over Earth history, which is reflected by their highly variable distribution between mantle and crustal reservoirs (Barnes et al., 1985; Day et al., 2016a; Puchtel and Humayun, 2005 and references therein). Therefore, the HSE systematics may provide a different type of information compared to that deconvolved from traditional radiogenic lithophile isotopic systems (Rb–Sr, Sm–Nd, Lu–Hf, U–Pb). Notably, there is a continuing discussion as to the effect of carbonatite melt metasomatism on HSE systematics of the Earth’s mantle rocks (Alard et al., 2011; Aulbach et al., 2014; Lorand et al., 2004; Reisberg et al., 2004). However, despite the wealth of carbonatite occurrences worldwide, a direct information on the behavior of HSE and Re–Os isotopic systematics in carbonatites is largely missing, with the exception of an incomplete HSE dataset for carbonatites from China reporting Ir, Ru, Rh, Pd and Pt abundances (Xu et al., 2008b) and a handful of Re–Os data reported for carbonatites from East Africa (Pearson et al., 1995), Gran Canaria (Widom et al., 1999), and Cape Verde (Escrig et al., 2005). Furthermore, it has been shown that some carbonatites associated with phoscorites, such as Phalaborwa, South Africa (Eriksson, 1989), or Ipanema, Brazil (Fontana, 2006), may contain considerable amounts of HSE and may thus be a potential source of these elements. To provide first order constraints on the behavior of the HSE and the Re–Os isotope system in carbonatites and to delimit the implications for metasomatic effects in the mantle, we determined HSE concentrations and Re–Os isotopic compositions in two well-characterized (Ackerman et al., 2017; Krátký et al., 2018) suites of carbonatites and associated silicate rocks (pyroxenites, monzogabbros, syenites) from south India, paralleled by sulfide petrography, because recent studies have shown that carbonatite metasomatism can mobilize at least Ir, Rh and Pt and redistribute them into neoformed sulfides (Akizawa et al., 2017).

3.2. Carbonatites and associated alkaline rocks in Tamil Nadu

The northern part of Tamil Nadu, South India, contains several occurrences of small Proterozoic carbonatite–silicate complexes (e.g., Hogenakal, Samalpatti, Sevattur, Pakkanadu–Malakkadu) located along the NE–SW trending Koratti and Attur shear zones (Grady, 1971; Srivastava, 1998). They are predominantly composed of large bodies of syenite and pyroxenite accompanied by calcite to magnesite-bearing carbonatites and silicocarbonatites intrusive into Proterozoic–Archean gneisses (Kumar et al., 1998; Schleicher et al., 1998; Viladkar and Subramanian, 1995), altogether exposed at deep erosional levels, resulting in the absence of clear indicators of tectonic settings. Nevertheless, the Koratti and Attur shear zones do not represent rifting zones and the absence of larger bodies of mafic alkaline (e.g., nephelinitic) rocks suggests that these complexes are not associated with a plume-related magmatism. Instead, their position within the shear zones, transecting older granitic rocks, as well as the association with syenites and pyroxenites make Tamil Nadu carbonatites comparable with,

for example, the Phalaborwa complex, South Africa (Frick, 1986; Groves and Vielreicher, 2001). Similarly, the late Mesozoic carbonatites surrounding the Tanzanian craton from the south and southwest, including Panda Hill, also appear to be emplaced along a shear zone (van Straaten, 1989). Therefore, this setting differs from more common occurrences of carbonatite complexes in plume-related within-plate setting, which may be either oceanic (Gran Canaria: Widom et al., 1999, Cape Verde Islands: Escrig et al., 2005) or in continental rifts (East African Rift: Bell and Simonetti, 1996; Bell and Tilton, 2001; Kalt et al., 1997; Pearson et al., 1995; Rhine Graben: Schleicher et al., 1990; Wang et al., 2014; Rio Grande Rift: McLemore and Moderski, 1990). It also differs from the carbonatites associated with large igneous provinces (e.g., Ernst and Bell, 2010; Simonetti et al., 1995; Viladkar and Wimmenaur, 1992).

Two spatially related complexes of Samalpatti and Sevattur (Supplementary Fig. S3.1) yield poorly defined K–Ar, Pb–Pb, and Rb–Sr isochron Neoproterozoic ages between 700 and 800 Ma (Kumar et al., 1998; Moralev et al., 1975; Schleicher et al., 1997). The Samalpatti complex comprises syenites, silicocarbonatites, carbonatites, pyroxenites, alkali gabbros, and serpentized dunites (Subramanian et al., 1978; Viladkar and Subramanian, 1995). The calcite carbonatites and silicocarbonatites (some of them being strikingly Mg–Cr-rich; Ackerman et al., 2017; Krátký et al., 2018) with a highly variable chemical composition usually form small bodies, lenses, and dykes in pyroxenites forming a discontinuous ring along a central syenite body (Srivastava, 1998). In comparison, the Sevattur complex is formed by calcite and magnesite carbonatite sandwiched between pyroxenites and syenites surrounded by gneisses (Schleicher et al., 1998; Viladkar and Subramanian, 1995). Previous investigations of major/trace element chemistry, paralleled by Sr–Nd–Pb–C–O isotopic data (Ackerman et al., 2017; Krátký et al., 2018), revealed that parental carbonatite melts at Samalpatti underwent significant modification through the interaction with the ambient crustal materials and post-magmatic hydrothermal alteration whereas the Sevattur carbonatite body was derived from enriched subcontinental lithospheric mantle sources without significant post-emplacement modifications (Ackerman et al., 2017; Schleicher et al., 1998).

3.3. Analytical methods

The concentrations of the HSE in bulk samples were determined at the Institute of Geology, The Czech Academy of Sciences. Prior to sample decomposition using a Carius tube technique (Shirey and Walker, 1995), the carbonate-rich (carbonatites and silicocarbonatites) matrix was decarbonized (e.g., Xu et al., 2008) to prevent tube explosion from internal overpressure.

To test for possible Os loss from CO₂-rich matrices during sample preparation, we performed four different decarbonation schemes using the COQ-1 carbonatite reference material (USGS) from Oka carbonatite, Canada. Approximately 2 g of COQ-1 was weighed into 60 ml Teflon beaker (Savillex). Subsequently, 1 ml 1 M HCl along with carefully weighted amounts of ¹⁹⁰Os, ¹⁸⁵Re, and ⁹⁹Ru–¹⁹¹Ir–¹⁰⁵Pd–¹⁹⁴Pt spikes were added. This step was made either at room temperature (*Scheme 1*) or with Teflon beakers cooled in dry ice (ca. -72°C) mixture (*Scheme 2*). In the *Scheme 3* and *4*, 1 ml of concentrated HBr was added drop-by-drop followed by 1 ml 1 M HCl +spikes mixture to ensure Os reduction in the solution at room temperature and in dry ice mixture, respectively. After vigorous reaction ceased, 4 ml 10 M HCl was added to ensure full decarbonation of the samples followed by additional 6 ml 10 M HCl. The solutions in sealed beakers were then equilibrated on a hot plate at 60°C for 24 hours. Following this step, samples were evaporated to dryness and the residue was transferred into Carius tubes in 4ml 10 M HCl. The results of these decarbonation tests indicate no systematic difference among the schemes used (Tab 3.1) and all observed variations in HSE concentrations can thus be attributed to the natural heterogeneity of the carbonatite, which would be highly susceptible to variable nugget effects given the low HSE abundances. This can be best illustrated using high but variable Re contents (0.68–0.89 ppb), most likely related to the presence of accessory sulfides in the COQ-1 powder (e.g., Treiman

Table 3.1. Highly siderophile element concentrations and ¹⁸⁷Os/¹⁸⁸Os isotopic data for COQ-1 Oka carbonatite reference material (USGS).

Decarbonization scheme	Re (ppb)	Re blank(%)	Os (ppb)	Os blank(%)	Ir (ppb)	Ir blank(%)	Ru (ppb)	Pt (ppb)	Pt blank(%)	Pd (ppb)	Pd blank(%)	¹⁸⁷ Re/ ¹⁸⁸ Os	2σ	¹⁸⁷ Os/ ¹⁸⁸ Os	2σ	¹⁸⁷ Os/ ¹⁸⁸ Os (120 Ma)
Scheme (1), only HCl	0.89	<0.1	0.0030	10	<0.005		<0.017	0.032	41.8	0.032	47.7	2090	220	3.6	0.47	neg
Scheme (2), HCl, cooled in dry ice	0.81	<0.1	0.0031	10	<0.005		<0.017	0.031	43.6	0.018	86.9	1792	178	3.42	0.43	neg
duplicate	0.74	<0.1	0.0031	10	<0.005		<0.017	0.035	38.4	0.035	44	1507	138	2.56	0.33	neg
Scheme (3), HCl + HBr mixture	0.69	<0.1	0.0030	10	<0.005		<0.017	0.026	51.2	0.042	36.6	1486	144	2.77	0.37	neg
duplicate	0.69	<0.1	0.0027	10	<0.005		<0.017	0.027	50.5	<0.015		1666	180	3.05	0.43	neg
Scheme (4), HCl + HBr mixture, cooled in dry ice	0.73	<0.1	0.0030	10	n.d.		<0.017	n.d.		0.02	76	1504	139	2.38	0.33	neg
duplicate	0.68	<0.1	0.0046	6	0.008	28.1	<0.017	0.039	34.8	<0.015		800	43	1.05	0.15	neg
n.d. – not detected.																

Tab. 3.1. Highly siderophile element concentrations and ¹⁸⁷Os/¹⁸⁸Os isotopic data for COQ-1 Oka carbonatite reference material (USGS).

and Essene, 1985). On the other hand, the overlap in determined Os abundance (3–5 ppt) and $^{187}\text{Os}/^{188}\text{Os}$ ratios in COQ-1 (except the sole value at $^{187}\text{Os}/^{188}\text{Os}$ of ~ 1.0) indicate that Os is most likely not volatilized during any of the decarbonation schemes employed. This suggests that either Os is present in reduced form in the sample or decarbonation has no oxidizing effect. For unknown carbonatite samples from this study, we consequently used the Scheme 1 using the sample amounts of $\sim 2\text{--}3\text{ g}$, while we note that an inherent advantage of using a dry ice mixture is slowing the vigorous reaction of sample with HCl and/or HCl+HBr.

Silicate rocks were directly weighed (1.3–2.5 g) and transferred into Carius tubes, followed by addition of 4 ml 10 M HCl and ^{190}Os , ^{185}Re , and ^{99}Ru – ^{191}Ir – ^{105}Pd – ^{194}Pt spikes. For both carbonatites and silicate rocks, 5 ml 14 M HNO_3 was added and the tubes were sealed, put into a metallic container, and placed into an oven at 230°C and 260°C for carbonate-rich and silicate rocks, respectively, for 72 hours.

Osmium was separated from *aqua regia* using CHCl_3 (Cohen and Waters, 1996) and purified by microdistillation (Birck et al., 1997). In case of silicate rocks, the remaining silica-rich residues after sample decomposition were re-dissolved in a mixture of concentrated HF–HCl (Ishikawa et al., 2014) to ensure full extraction of remaining HSE from the matrix. Iridium, Ru, Pd, Pt, and Re were separated from the matrix using anion-exchange chromatography and their concentrations were measured using an *Element 2* coupled with an Aridus II (CETAC) desolvating nebulizer, housed at the Institute of Geology of the Czech Academy of Sciences, using standard Ir, Ru, Pd, Pt and Re solutions for mass bias corrections. The in-run precision of the measured isotopic ratios was always better than $\pm 0.5\%$ (2SD). Total procedural blanks were <2 pg Re, 0.4–0.8 pg Os, 2–7 pg Ir, 10–24 pg Ru, 12–42 pg Pt, and 14–48 pg Pd, respectively. The blank contributions (in %) for all HSE are given in Tabs 3.1. and 3.2. The COQ-1 reference material contains very low HSE contents (except Re with negligible blank contribution) resulting in the blank corrections exceeding 87% in some cases (note that all Ru measurements and all but one Ir analysis are below the detection limit). On the other hand, the blank corrections for most of the unknown samples (except Ru which is mostly below the detection limit) did not exceed 15%, but several samples extremely depleted in HSE required blank corrections of up to 66% (e.g., IC06D for Ir, Pt and Pd; Tab 3.2). Osmium isotopic compositions were determined using a *Finnigan MAT 262* mass spectrometer, housed at the Czech Geological Survey, with N-TIMS technique (Creaser et al., 1991a; Völkening et al., 1991) using single Pt filaments, concentrated HBr for sample loading and $\text{Ba}(\text{OH})_2$ activator with continuous bleeding of O_2 for negative ion production. All samples and blanks were analyzed in a peak hopping mode using an electron multiplier. The measured Os isotopic ratios were corrected offline for different oxide isobaric interferences, spike/blank contribution followed by instrumental mass fractionation correction using $^{192}\text{Os}/^{188}\text{Os}$

=3.08271 (Shirey and Walker, 1998). The in-run precision of $^{187}\text{Os}/^{188}\text{Os}$ measurements was always better than $\pm 0.4\%$ (2SE).

To evaluate the veracity of the obtained Re–Os data, the propagated uncertainties for $^{187}\text{Re}/^{188}\text{Os}$, measured/initial $^{187}\text{Os}/^{188}\text{Os}$, and γOs have been calculated and are listed in Tabs 3.1. and 3.2. (note that COQ-1 reference material yielded a negative initial $^{187}\text{Os}/^{188}\text{Os}$, most likely due to late-stage perturbation of the Re–Os system). These calculations include all major sources of the uncertainty, i.e. the errors on the Re–Os spike calibration, mass spectrometry analyses, blank correction (using average blank throughout the study and its uncertainty), age, and decay constant.

Table 3.2.

Highly siderophile element concentrations and Re–Os isotopic data for carbonatites and associated alkaline rocks from Tamil Nadu, India.

Sample	Rock	FeO (wt.%) ^a	S (wt.%) ^a	Re (ppb)	Re blank(%)	Os (ppb)	Os blank(%)	Ir (ppb)	Ir blank(%)	Ru (ppb)	Ru blank(%)	Pt (ppb)	Pt blank(%)	Pd (ppb)	Pd blank(%)	¹⁸⁷ Re/ ¹⁸⁸ Os	2σ	¹⁸⁷ Os/ ¹⁸⁸ Os	2σ	¹⁸⁷ Os/ ¹⁸⁸ Os (800 Ma)	2σ	¹⁸⁷ Os/ ¹⁸⁸ Os yOs(800 Ma)
Samalpatti																						
IC05A	carbonatite	0.78	0.024	0.181	0.3	0.085	0.3	0.012	15.1	<0.017		0.091	11.9	0.14	8.9	10.58	0.09	0.387	0.007	0.245	102	43
IC05F1	carbonatite	0.46	0.12	0.007	13.4	0.013	2.2	0.005	44.6	0.027	31.2	0.29	4.6	0.29	5.3	2.9	0.42	1.34	0.04	1.3	970	186
IC03A	Mg–Cr-rich silico- carbonatite	1.35	<0.010	0.008	12.3	0.18	0.2	0.06	3.9	0.18	4.8	15.2	0.1	2.34	0.7	0.22	0.03	0.183	0.002	0.18	48	12
	duplicate			0.01	7.5	0.23	0.1	0.08	2.8	0.2	4.3	14.8	0.1	1.27	1.2	0.2	0.02	0.18	0.001	0.177	46	11
IC03B	Mg–Cr-rich silico- carbonatite	1.18	<0.010	0.029	1.7	0.16	0.1	0.049	2.3	0.23	1.8	32.7	<0.1	3.41	0.2	0.92	0.02	0.164	0.001	0.152	25	7
IC03D	Mg–Cr-rich silico- carbonatite	0.94	<0.010	0.013	3.9	0.009	1.7	0.071	1.6	0.23	1.8	38	<0.1	2.79	0.3	7.31	0.55	0.46	0.05	0.364	199	122
IC03E	Mg–Cr-rich silico- carbonatite	1.70	<0.010	0.008	12.4	0.23	0.1	0.053	4.2	0.22	3.8	19.5	0.1	0.66	2.3	0.16	0.02	0.153	0.001	0.151	24	6
IC04A	Mg–Cr-rich silico- carbonatite	1.18	0.02	0.006	15.3	0.36	0.1	0.46	0.5	0.35	2.4	12.5	0.1	0.38	4.1	0.08	0.01	0.145	0.001	0.144	18	4
IC06E	Mg–Cr-rich silico- carbonatite	1.35	0.026	0.003	6.8	0.1	0.1	0.12	1	0.26	1.6	0.63	0.1	0.12	6.6	0.17	0.02	0.574	0.002	0.57	370	51
IC06D	feritized pyroxenite	7.97	0.016	0.021	3.6	0.004	12.1	0.006	59.8	<0.017		0.04	52.7	0.036	66.1	36	5	2.73	0.32	2.2	1749	485
IC07D	pyroxenite	4.33	<0.010	0.019	2.6	0.33	0.1	0.032	7.2	0.21	4.0	10.9	0.1	2.25	0.7	0.28	0.02	0.174	0.001	0.171	40	9
IC07E	monzogabro	0.22	<0.011	0.019	2.5	0.003	5.3	0.006	17.9	<0.017		0.15	4.4	0.11	6.8	37	2	1.05	0.06	0.6	356	175
IC09	syenite	0.23	0.073	0.014	3.5	0.002	16.2	0.038	6.3	<0.017		0.15	9.3	0.071	23.1	42	7	1.61	0.28	1	753	396
Sevattur																						
IC10A	carbonatite	0.61	0.015	0.015	3.4	0.016	0.9	<0.005		<0.017		0.2	3.4	0.13	5.8	4.44	0.16	0.186	0.008	0.2166	4	3
IC10J	carbonatite	1.42	0.017	0.057	1.1	0.19	0.1	0.012	15.0	<0.017		0.1	10.5	0.50	2.5	1.47	0.03	0.45	0.02	0.43	252	94
	duplicate			0.068	0.4	0.097	0.3	0.011	20.6	<0.017		0.25	5.4	0.56	2.8	3.71	0.07	0.90	0.02	0.85	603	117
IC11A	mt-carbonatite	1.36	0.013	0.984	<0.1	0.051	0.5	<0.005		<0.017		<0.024		0.2	6.1	217	14	10.4	1.3	7	6052	1168
IC16A	carbonatite	1.10	<0.010	0.002	22.1	0.12	0.2	<0.005		<0.017		0.12	8.8	0.26	4.8	0.10	0.03	0.41	0.02	0.410	237	83
IC16B	carbonatite	1.72	n.d.	0.011	5.5	0.24	0.1	<0.005		<0.017		0.069	19.4	<0.015		0.22	0.02	0.124	0.002	0.124	0.1	0.1
IC11B	magnetite	24.8	n.d.	0.011	5.5	0.011	3.7	0.014	21.4	<0.017		0.35	5.1	0.069	29.9	5.7	0.7	1.34	0.05	1.3	939	201
IC13A	monzogabro	2.17	0.017	0.283	0.2	0.018	0.9	<0.005		0.063	6.7	0.92	0.7	0.78	1.0	106	1	2.99	0.03	1.6	1183	251
IC14	qtzmonzogabro	0.61	0.031	0.043	1.2	0.010	5.0	<0.005		<0.017		0.47	4.7	0.085	30.2	34	2	4.8	0.3	4.4	3494	579

n.d. – not detected, yOs value calculated using chondrite composition of Shirey and Walker (1998). ^aData from Ackerman et al. (2017).**Tab. 3.2.** Highly siderophile element concentrations and Re–Os isotopic data for carbonatites and associated alkaline rocks from Tamil Nadu, India

3.4. Results

3.4.1. Sulfur concentrations and petrography of sulfides and oxides

Two carbonatites IC05A and IC05F1 from Samalpatti with a large difference in sulfur concentrations (0.024 and 0.12 wt.%, respectively) are associated with a rare abundance of sulfides in the former and their common presence in the latter. Sulfides are exclusively represented by pyrite with typical pale-yellow color in reflected light. Most grains are interstitial with <200µm diameter and apparent association to silicate phases, mostly pyroxene (Fig.3.1a). Only a few pyrites are in the form of immiscible blebs (<20µm) and these are enclosed in other opaque minerals or in calcite. In both samples, rare magnetite grains commonly replaced by hematite are present. The carbonatites from Sevattur have generally low sulfur contents (<0.017wt.%) and small (<15µm) sulfides represented by pyrite were found only in sample IC10J. In contrast, most samples are rich in magnetite forming predominantly euhedral individual dispersed grains up to 8 mm large, commonly resorbed, recrystallized, and replaced by hematite (Fig.3.1b) or filling the cracks in carbonates. Ilmenite is also present.

Magnesium–Cr-rich silicocarbonatites from Samalpatti have sulfur contents mostly below the detection limit of 0.010 wt.%, with samples IC04A and IC06E reaching up to 0.03 wt.% (Tab 3.1). Sulfides are rare in all examined samples and only scarce and small (<20µm) interstitial pyrite was found (Fig.3.1c). All samples contain abundant magnetite replaced by hematite (up to 200µm; e.g., Fig.3.1c), which mostly has skeletal structure.

Concentrations of sulfur in silicate rocks from both localities are highly variable ranging from 0.02 to 0.13 wt.%; the latter was found in monzogabbro IC06A from Samalpatti. In all samples, pyrite was the sole sulfide phase found. It usually forms individual interstitial grains of a variable size (<30 to ~200µm), in association with Fe–Ti oxides (magnetite, hematite) and titanite (Fig.3.1d).

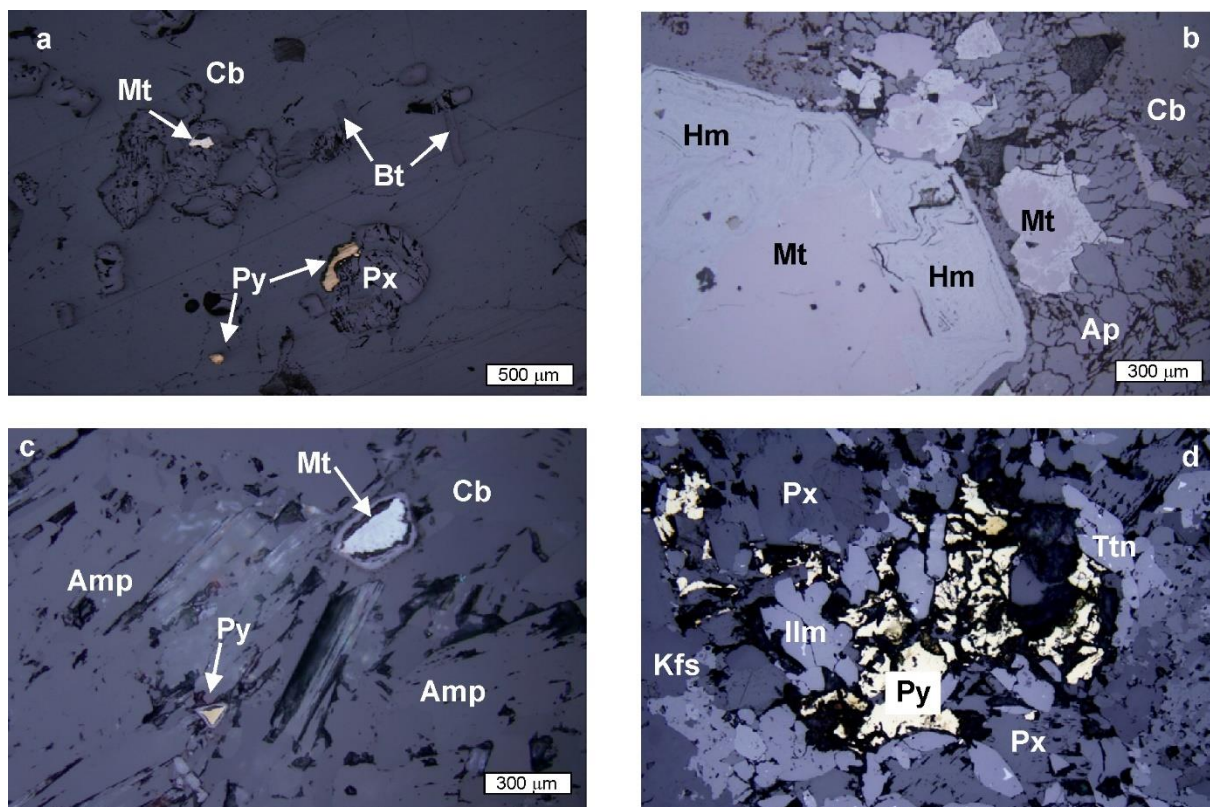


Fig. 3.1. Microphotographs of sulfides and oxides in the Tamil Nadu samples (reflected light). (a) Pyrite (Py) intergrowths with pyroxene (Px) and Py interstitial grains enclosed within carbonate (Cb) matrix. Magnetite (Mt) is mostly associated with silicate phases such as pyroxene or biotite (Bt) – carbonatite IC05F1. (b) Hematite (Hm) replacing large grains of magnetite (Mt) – magnetite-rich calcicarbonatite IC11A. (c) Rare grain of pyrite (Py) found in amphibole (Amp)-carbonate (Cb) matrix of Mg–Cr-rich silicocarbonatite IC03B. (d) Large pyrite (Py) intergrowths with ilmenite (Ilm) and titanite (Ttn) – monzogabbro IC06A.

3.4.2. Highly siderophile element concentrations and Re–Os isotopic systematic

The Samalpatti and Sevattur calcicarbonatites have low HSE contents ($\Sigma\text{HSE} < 1.22$ ppb) with I-PGE (Os, Ir, Ru) concentrations < 0.20 ppb (Os, Ir) whereby Ru is below the detection limit in almost all cases (Tab 3.1). From the P-PGE group, Pt and Pd contents are rather uniform and vary from 0.091 to 0.29 ppb and 0.13 to 0.56 ppb, respectively. In contrast, Re exhibits an extreme degree of variation from 0.006 to 0.984 ppb, with $[\text{Re}] < 0.1$ ppb for most samples. No significant covariation between HSE and sulfur contents is observed (Fig. 3.2). Carbonatites from both localities exhibit similar, overlapping primitive mantle-normalized HSE patterns (Fig. 3.3a) with steady enrichments from Ir to Pd and $\text{Pd}_\text{N}/\text{Ir}_\text{N}$ ratios from 5.8 to 28, similar to those found in carbonatites from China (Cheng et al., 2003; Xu et al., 2008b). The carbonatites are systematically enriched in Os over Ir, with $\text{Os}_\text{N}/\text{Ir}_\text{N} = 2.3$ –15. Except Pt and Os, the HSE abundances are below those reported for mid-ocean ridge basalts (MORB; Bézou et al., 2005; Gannoun et al., 2007), primitive upper mantle (PUM; (Day et al., 2017)) or oceanic island basalts (OIB; Day et al., 2013, 2010; Fig. 3.3a).

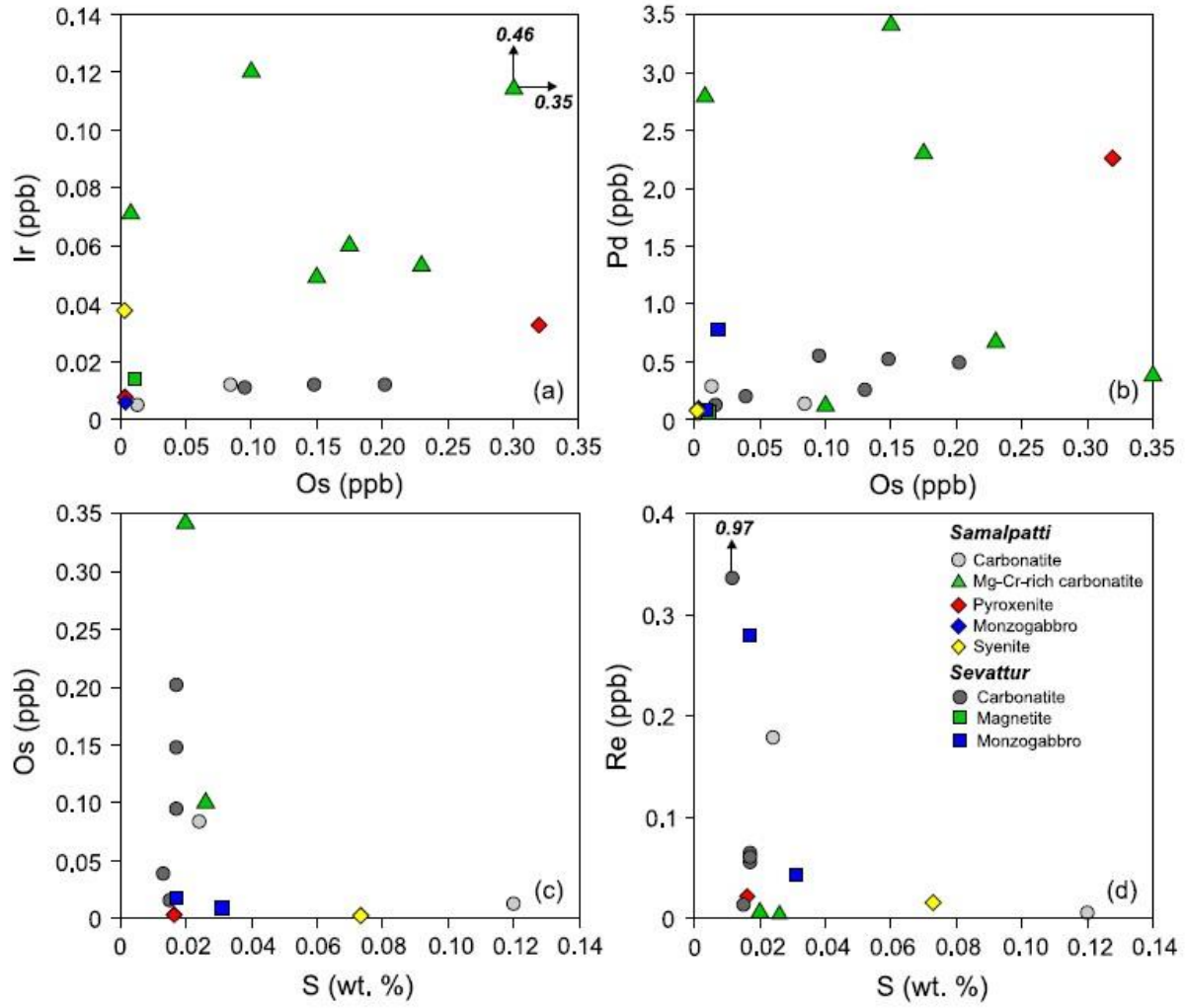


Fig. 3.2. Binary plots of inter-distribution of Os, Ir, and Pd (a, b), and the relationship between Os and Re versus total sulfur (c, d). Note the absence of positive correlations between Os and Ir for carbonatites indicating different behavior of the I-PGE. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

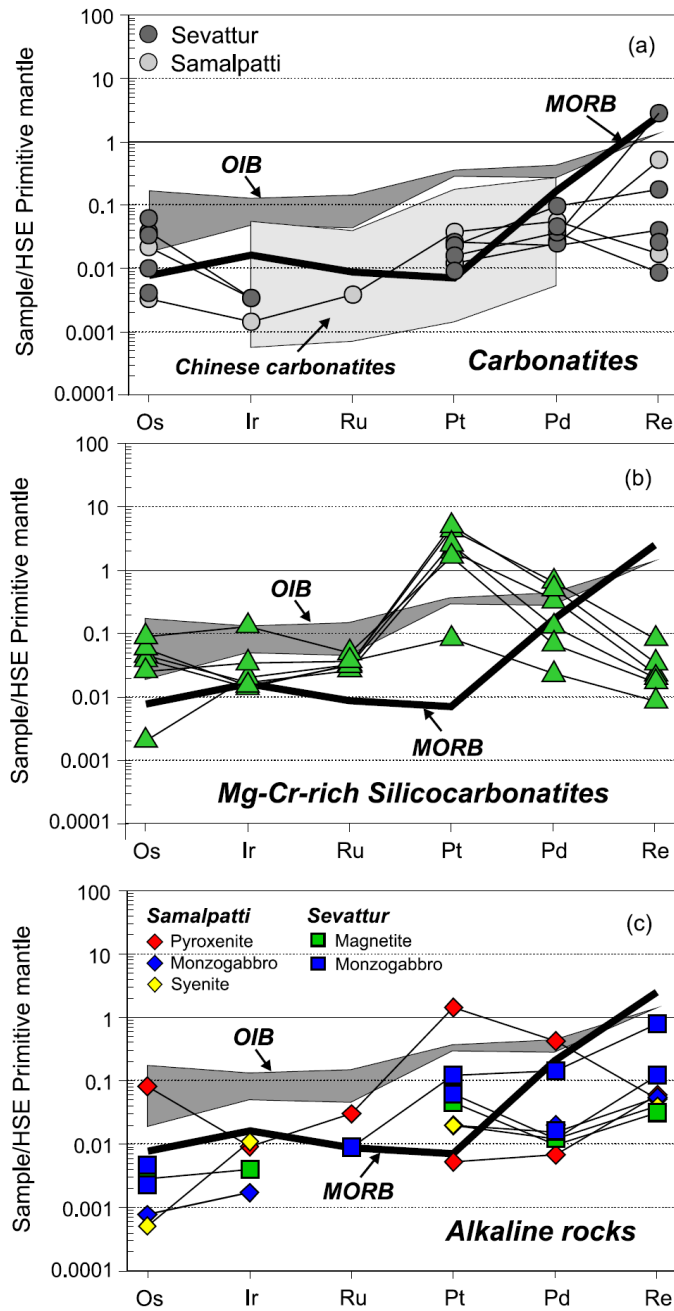


Fig. 3.3. Primitive mantle-normalized normalized HSE distributions in (a) calcicarbonatites, (b) Mg–Cr-rich silicocarbonatites, and (c) associated silicate rocks. Normalizing values are taken from Day et al. (2017). The values for MORB are from Bézous et al. (2005) and Gannoun et al. (2007); the values for OIB are from Ireland et al. (2009) and Day et al. (2010).

ppb, paralleled by low Re abundances (<0.029 ppb) with a negative slope of PM-normalized patterns (Fig. 3.3b) and PdN/ReN ratios between 2.0 and 25. Three out of five Mg–Cr-rich silicocarbonatites

The Re–Os isotopic compositions of Samalpatti and Sevattur carbonatites are extremely variable ranging from only slightly to highly radiogenic present-day $^{187}\text{Os}/^{188}\text{Os}$ values (0.186–10.4) and $^{187}\text{Re}/^{188}\text{Os}$ from 0.10 to 217 (Fig. 3.4). Consequently, the initial γOs values (back-calculated to 800 Ma) vary from +0.1 to +6052 (Tab 3.2; Fig. 3.5). Duplicate analysis of carbonatite IC10J revealed that natural heterogeneity of HSE concentrations in carbonatites is similar to other mantle-derived rocks (e.g., peridotites, basalts), but there is a significant $^{187}\text{Os}/^{188}\text{Os}$ variation (0.43 and 0.86; Tab 3.2) compared with mafic silicate lithologies. The magnetite fraction (IC11B) yields HSE contents similar to or lower than the host Sevattur carbonatite (IC11A).

The HSE contents in Mg–Cr-rich silicocarbonatites are systematically higher ($\Sigma\text{HSE} = 14\text{--}41$ ppb, except sample IC06E with $\Sigma\text{HSE} = 1.2$ ppb). With the exception of sample IC03D showing anomalously low Os (0.009 ppb), the rocks exhibit elevated I-PGE contents similar to OIB-like melts, with a moderate degree of fractionation (e.g., $\text{Os}_\text{N}/\text{Ir}_\text{N} = 0.7\text{--}3.9$; Fig. 3.3b). Further, they also are markedly enriched in Pt (up to 38 ppb) displaying positive Pt anomalies ($\text{Pt}_\text{N}/\text{Ir}_\text{N} = 2.4\text{--}307$; Fig. 3.3b). Palladium contents vary widely from 0.12 to 3.4

yield a narrow range of superchondritic present-day $^{187}\text{Os}/^{188}\text{Os}$ values from 0.145 to 0.183 resulting in $\gamma_{\text{Os}_{800\text{Ma}}}$ values between +18 and +48; duplicate analysis of IC03A suggests only minor sample heterogeneity in terms of HSE contents and $^{187}\text{Os}/^{188}\text{Os}$ (Tab 3.2). Two Mg–Cr-rich silicocarbonatites IC03D and IC06E exhibit more radiogenic compositions with present-day $^{187}\text{Os}/^{188}\text{Os}$ of 0.46 and 0.574, respectively and the $\gamma_{\text{Os}_{800\text{Ma}}}$ of +199 and +370, respectively (Fig. 3.5).

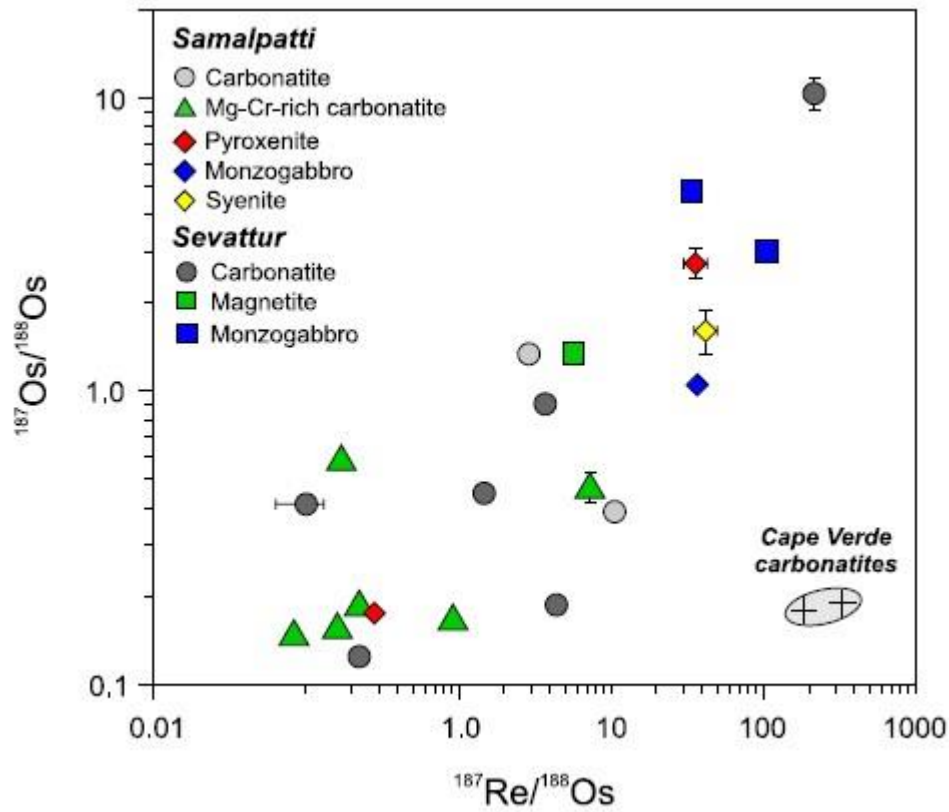


Fig. 3.4. The $^{187}\text{Re}/^{188}\text{Os}$ versus present-day $^{187}\text{Os}/^{188}\text{Os}$ ratios of the Tamil Nadu carbonatites, silicocarbonatites, and associated alkaline rocks (note logarithmic scales on both axes). The Re–Os isotopic compositions of two carbonatites from the Cape Verde Islands are from (Escrig et al., 2005). The combined uncertainties are represented by 2σ values, but note that most of them are smaller than the symbol size.

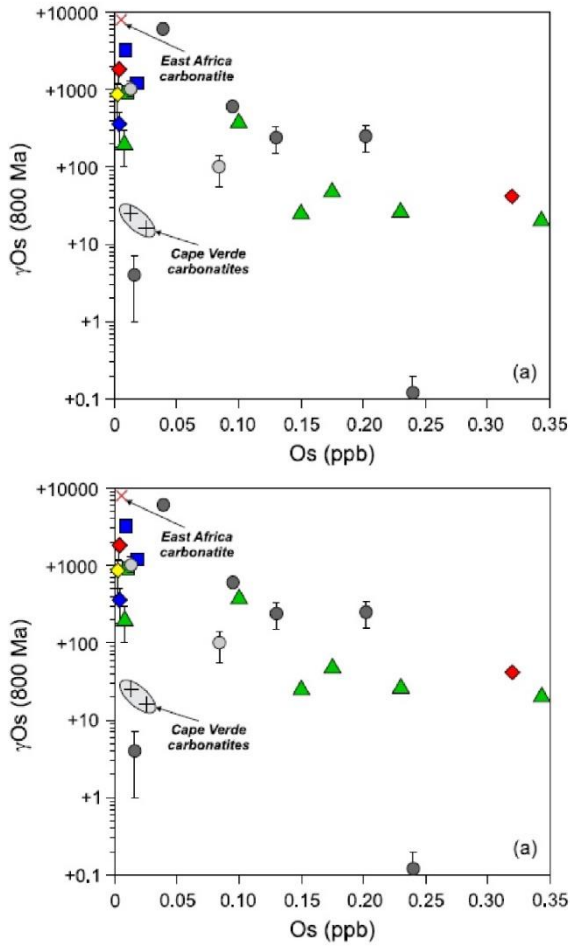


Fig. 3.5. Osmium (a) and Pt (b) concentrations versus γOs values calculated at 800 Ma for the Tamil Nadu suite from this study (note that only carbonatites are plotted in the panel b for clarity). Platinum is well-correlated with γOs , indicating the pre-dominant source of Pt as coming from a recycled crustal lithology. The combined uncertainties are represented by 2σ values, but note that most of them are smaller than the symbol size. Data for two carbonatites from the Cape Verde Islands and one carbonatite from the East African rift are from Escrig et al. (2005) and Pearson et al. (1995), respectively.

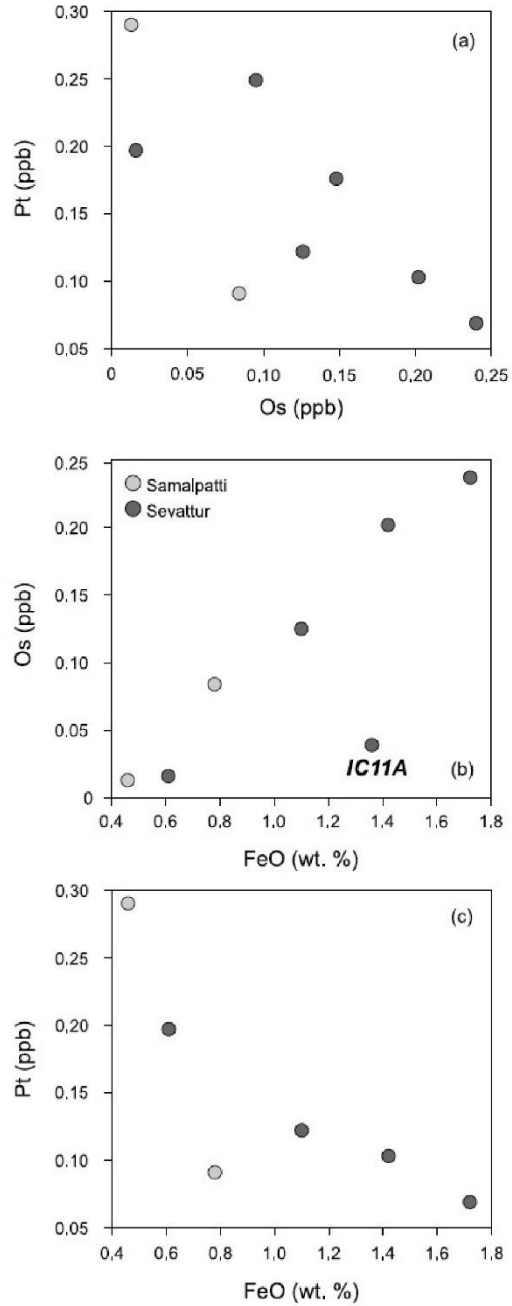


Fig. 3.6. Co-variations between Os and Pt (a) and Pt–Os with FeO concentrations (b, c) for Tamil Nadu calciocarbonatites (FeO data from Ackerman et al., 2017). Note the excellent correlations found for Os versus FeO ($r=0.99$; when magnetite-rich sample IC11A is omitted) and Pt versus FeO ($r=0.79$).

The silicate rocks (pyroxenites, monzogabbros, syenite) from both localities have similarly low and largely overlapping HSE contents ($\Sigma\text{HSE} < 2.3$ ppb) with PM-normalized distribution typical for crustal-derived rocks (steady enrichment from Os to Re; Fig. 3.3c). The pyroxenite IC07D from Samalpatti is characterized by a highly fractionated HSE pattern with predominance of Os over Ir ($\text{Os}_\text{N}/\text{Ir}_\text{N}=9.0$) and high Pt content (11 ppb) forming a significant positive Pt anomaly in the PM-normalized plot (Fig. 3.2c). In general, the silicate rocks from Sevattur tend to have more radiogenic present-day $^{187}\text{Os}/^{188}\text{Os}$ and $\gamma\text{Os}_{800\text{Ma}}$ values than those from Samalpatti (Tab 3.2; Fig. 3.5). The study of Day et al. (2016b) emphasized, that during the desilicification procedure used also in this study, Re/Os of the samples could be modified due to additional recovery of Re from silicate sludge leading to the higher calculated $^{187}\text{Re}/^{188}\text{Os}$. However, even if the Re contents are overestimated by 50%, the uncertainty on the calculated $\gamma\text{Os}_{800\text{Ma}}$ is identical within the uncertainty range given in Tab 3.2.

3.5. Discussion

3.5.1. Controls and nature of HSE distribution in carbonatites

Sparse data exist on the HSE contents of mantle-derived carbonatite magmas. The available information includes PGE data from REE-rich and barren carbonatites of Paleocene age (65–45 Ma) from China (Cheng et al., 2003; Xu et al., 2008b), formed in rift-related as well as continental collision zone, and an incomplete dataset from prominent fault-related phoscorite-carbonatite complexes with PGE mineralization from Brazil (123–70 Ma) and South Africa (~2.0 Ga; Fontana, 2006). These studies reported on a large range of HSE contents from ppt (Chinese carbonatites) to ppm levels (e.g., up to 3,200 ppb for Pt; 1,330 ppb for Pd; 13,500 ppb for Ir; Fontana, 2006); i.e., more than six orders of magnitude differences may exist. Such enormous variability can result from either the early separation of sulfide-rich melts leading to the strong HSE depletion (Xu et al., 2008b), transport of HSE through the volatile-rich melts/fluids causing moderate HSE enrichments (Cheng et al., 2003), or accumulation of HSE at even economic grade caused by a combination of mafic melt differentiation and post-magmatic evolution (Fontana, 2006).

In mantle-derived rocks (e.g., peridotites, basalts), the HSE are predominantly associated with Fe–Ni–Cu sulfides with $D_{\text{sulfide/silicate}}$ values for all HSE typically in the range of 10_3 (Re) to 10_7 (I-PGE) (Brenan et al., 2016; Crocket et al., 1997; Mungall and Brenan, 2014) and the extent of HSE enrichment is thus linked to sulfur content in the magma source, sulfur saturation of the melts and the amount of residual sulfides retained in the mantle during melting. Experiments have shown that solubility of sulfur in basaltic melts decreases exponentially with increasing pressure and that basaltic melts become S-undersaturated during their ascent (Mavrogenes and O'Neill, 1999), unless significant

melt fractionation and/or assimilation of S-rich sediments occur. Furthermore, sulfur saturation is much higher (1–2 wt.% S) in oxidized melts ($fO_2 > +2$ FMQ; presence of sulfates) than in those with $fO_2 < -1$ FMQ (presence of sulfides; Mavrogenes and O'Neill, 1999); in parallel, it also increases with the increasing FeO content of the melt (O'Neill and Mavrogenes, 2002). For carbonatite melts, however, the experimental studies on sulfur solubility are rare. (Helz and Wyllie, 1979) have shown that FeO-free carbonatite magma at 1 kbar can dissolve up to 0.9 wt.% S. Recent preliminary experiments of Jorgenson (2017) indicate that sulfur solubility in carbonatite magmas is nearly an order of magnitude higher than in silicate melt, but that the behavior of sulfur in silicate and carbonatite melt is broadly similar, with a decreasing solubility from 1 to 2 GPa (0.08–0.5 and 0.01–0.15 wt.% S, respectively) and increasing solubility with increasing FeO content of the carbonatite melt.

The Tamil Nadu carbonatites are characterized by variable sulfur contents (<0.01 to 0.12 wt.%), paralleled by mostly absent (Sevattur) to common (Samalpatti) interstitial pyrite, which were most likely precipitated directly from the carbonatite melt because they are enclosed directly in carbonate grains and/or intimately associated with silicates or Fe–Ti oxides (Fig. 3.1). This indicates rather S-undersaturated conditions during the melt emplacement in case of the Sevattur carbonatites whereby a common presence of magnetite argues for high oxygen fugacity. In contrast, the Samalpatti carbonatites are characterized by a common presence of pyrite, which indicates high sulfur fugacity (cf. Lorand and Grégoire, 2006) and S-saturation of the melt. This can be enhanced by sizeable contamination of carbonatite melt by S-enriched ambient crustal (most likely metasedimentary) materials as evidenced from coupled Sr–Nd–C–O systematics of the Samalpatti suite (Ackerman et al., 2017).

Silicate melts that are formed by low to moderate (~ 1 to 25%) degrees of partial melting of mantle (e.g., MORB and OIB-like basalts, kimberlites) are S-saturated, thus leaving behind residual sulfides (e.g., Hamlyn et al., 1985; Mitchell and Keays, 1981). Consequently, this process leads to a large HSE depletion observed in these magmas (e.g., Bézoz et al., 2005; Day et al., 2010; Gannoun et al., 2007; Ireland et al., 2009) due to the overall high $D_{\text{sulfide/silicate}}$ for HSE (Mungall and Brenan, 2014). As noted above, carbonatitic magmas represent low-degree (<0.3%) partial melts which should likely be S-saturated at the source. Hence, they are predicted to be largely impoverished in HSE which is in agreement with the observed low HSE contents ($\Sigma\text{HSE} < 1.2$ ppb) in the Tamil Nadu carbonatites compared to mantle-derived basaltic melts (Fig. 3.3). Alternatively, progressive magmatic fractionation of parental carbonatite melts as indicated by variable FeO contents could lead to an increased solubility of sulfur. This process would, in turn, promote separation of S-rich melts extracting the HSE bud-get from the primary carbonatite melt. Furthermore, extremely low HSE contents can be partly connected with the nature of the melt source, which may contain an HSE-poor, crustal recycled lithology (e.g., eclogite, pyroxenite) as discussed below.

In contrast, the HSE patterns of Tamil Nadu carbonatites show some important differences compared to silicate melts (e.g., high Os/Ir, very low Ru), which can be related to different HSE partitioning between carbonatitic melts and residual sulfide. Jorgenson (2017) determined the partitioning coefficients of HSE between monosulfide solution (Mss) and FeO-bearing (~4 wt.%) carbonatite melt showing that $D_{\text{Mss/carb}}$ for Pt is two orders of magnitude higher than $D_{\text{Mss/sil}}$ ($\sim 10^4$ vs. 10^2) while $D_{\text{Mss/carb}}$ for Os and Ir are one to two orders of magnitude lower than those reported for Mss/silicate melt ($\sim 10^5$ for Os and 10^6 for Ir vs. 10^7 for both elements). Thus, in S-saturated carbonatite magmas, I-PGE will be more efficiently sequestered into melt in comparison with Pt. This behavior is illustrated by the broadly negative correlation between Os and Pt found for the Tamil Nadu carbonatites (Fig. 3.6a). Further-more, a striking feature of Tamil Nadu carbonatites is the systematic and significant enrichment of Os over Ir ($\text{Os}_\text{N}/\text{Ir}_\text{N}=2.3\text{--}15$), which is opposite to that observed for basaltic melts ($\text{Os}_\text{N}/\text{Ir}_\text{N}<1$; Gannoun et al., 2016 and references therein). Interestingly, this appears to be complementary to low $\text{Os}_\text{N}/\text{Ir}_\text{N}<1$ typically observed in off-craton mantle xenoliths (Lorand et al., 2013; Luguet and Reisberg, 2016 and references therein), which may be indicative of selective dissolution of the I-PGE carriers (alloys, high-temperature sulfides) during percolation of oxidized carbonatitic or carbonated silicate melts in the mantle (cf. Aulbach et al., 2016). Also, FeO contents (ferrous iron determined by wet analysis) of Tamil Nadu bulk carbonatites show an excellent positive correlation with [Os] if magnetite-rich carbonatite IC11A is omitted (Fig. 3.6b), and broadly negative correlation with [Pt] (Fig. 3.6c). This likely indicates that FeO exerts control on distribution of Os and Pt in carbonatite magmas during fractional crystallization while for other HSE elements the relationships are less clear, partly as a consequence of too low abundances (Ir, Ru).

The high Re content in sample IC11A (0.97 ppb) cannot be associated with elevated modal proportion of magnetite (6 vol.%) because magnetite IC11B separated from the same sample only contains a subordinate proportion of Re (0.011 ppb; Tab 3.2). The new data also indicates that magnetite does not carry significant amounts of I-PGE as suggested from experimental studies (Capobianco et al., 1994). Therefore, the HSE are probably hosted by rare and heterogeneously dispersed micro-and/or nano-phase sulfides or other HSE-bearing phases (e.g., alloys, tellurides; Lorand and Luguet, 2016) or some yet-unidentified mineral phase.

3.5.2. Insights into carbonatite mantle sources from the Re–Os isotopic systematic

Mantle-derived carbonatites and carbonated silicate melts typically are suggested to form by low partial melting degrees of carbonated peridotite, eclogite, or a mixed source at depths corresponding to 2–3 GPa (Dasgupta and Hirschmann, 2006; Hammouda, 2003; Nelson et al., 1988; Wallace and Green, 1988). In this respect, the Re–Os isotopic systematics can serve as a powerful and sensitive tracer of a melt source in comparison to lithophile element isotopic systematics (e.g., Sr–Nd) because

mantle peridotites commonly yield non-radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotopic signature (<0.13 ; (Aulbach et al., 2016; Becker and Dale, 2016; Luguet and Reisberg, 2016; Shirey and Walker, 1998 and references therein) while recycled crustal lithologies (pyroxenites, eclogites) can have extremely radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values (up to ~ 16 , Ackerman et al., 2016; Becker, 2000; van Acken et al., 2010; Wang and Becker, 2015). Nevertheless, the reported Re–Os isotopic compositions of carbonatites so far are extremely rare, sometimes incomplete, and show large variations. This includes a single datum from Uganda, East Africa (Pearson et al., 1995) with extremely high $^{187}\text{Re}/^{188}\text{Os} = 6130$ and initial γOs of $+7,198$, sole Os data for two oceanic carbonatites from Gran Canaria (0.005 and 0.015 ppb Os and present-day $^{187}\text{Os}/^{188}\text{Os}$ of 0.46 and 0.61, respectively; Widom et al., 1999) and two oceanic carbonatites from Cape Verde Islands ($^{187}\text{Re}/^{188}\text{Os}$ of 184 and 343, and initial γOs of $+16$ and $+26$, respectively; Escrig et al., 2005). In this respect, the Re–Os isotopic composition of the Tamil Nadu carbonatites from this study can provide more detailed observations on the nature of carbonatite melt sources with respect to their $^{187}\text{Os}/^{188}\text{Os}$.

With the exception of magnetite-rich carbonatite IC11A, the other samples returned age-corrected values close to those measured owing to the low Re/Os. The calculated $\gamma\text{Os}_{800\text{Ma}}$ values of these carbonatites show a large variation from $+0.1$ to $+970$, with no relationship to the initial isotopic values of lithophile elements ($^{87}\text{Sr}/^{86}\text{Sr}$, ϵNd , $^{206}\text{Pb}/^{208}\text{Pb}$ – not shown) or [Os] (Fig. 3.5a). This range of γOs values cannot be ascribed to either pre-emplacement crustal contamination because ambient silicate rocks from Tamil Nadu have similar or only slightly higher γOs values between 40 and 3,494 (Tab 3.2) or possible Re loss during carbonatite melt degassing (cf., Bennett et al., 2000) because Os is even more compatible in gas condensates (Yudovskaya et al., 2008). Furthermore, fenitized pyroxenite IC06D which documents pervasive overprint by alkalis released from the carbonatitic magmas and, therefore, a possible fluid-assisted element transfer, contains much less Os than the associated carbonatites while Re content is similar (Tab 3.2, Fig. 3.2). Whilst mafic lower crustal rocks can bear extreme γOs signatures (up to $\sim 19,000$; Aulbach et al., 2010), variable mixing with such lithologies must be accompanied by enrichments in SiO_2 and variability in ϵNd none of which is observed in the carbonatite suite. Thus, the Re–Os isotopic composition rather reflects that of the source of carbonatite melts and require a recycled crustal component to explain highly radiogenic $\gamma\text{Os}_{800\text{Ma}}$ values. No clear mixing trend is developed between [Os] and γOs , which can be associated with highly variable combined uncertainties and modest Os elemental heterogeneity observed in the duplicate analysis (IC10J; Tab 3.2). However, it is evident that carbonatites with high Os contents tend to have lower γOs values (Fig. 3.5a). In addition, high γOs values are coupled with Pt enrichments as can be recognized from well-developed positive co-variation (Fig. 3.5b). This indicates that the Tamil Nadu carbonatite parental magmas were formed by melting of a heterogeneous mantle source with pre-dominance of two components – depleted peridotite with $\gamma\text{Os} \leq 0$ and $\text{Pt}/\text{Os} < 1$, and recycled crust (eclogite?) with

$\gamma\text{Os} > 100$ and $\text{Pt}/\text{Os} > 10$, whereby the presence of the latter component is further supported by radiogenic $^{87}\text{Sr}/^{86}\text{Sr}_{800\text{Ma}}$ (0.7052–0.7075) and low $\epsilon\text{Nd}_{(800\text{ Ma})}$ values between –14.4 and –7.0 reported for the Tamil Nadu carbonatites (Ackerman et al., 2017). Although the exact composition of these two components cannot be constrained more accurately and the latter end member can be extremely variable in both signatures, it is still best characterized by notably high Pt/Os and highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ signature (e.g., Aulbach et al., 2016; Luguet et al., 2008; Penniston-Dorland et al., 2012). While we note that the uncertainty associated with such an end member is large, the best fit to explain the new data from this study would be a simple mixing scenario between two hypothetical end-members with given compositions (depleted mantle [A] – $\gamma\text{Os} = 0$ and $\text{Pt}/\text{Os} = 0.4$, eclogite [B] – $\gamma\text{Os} = \sim 1000$ and $\text{Pt}/\text{Os} = 30$). Using this approach, the composition of most Tamil Nadu carbonatites can be explained by a carbonated peridotite source with <10% of recycled component, with only carbonatite IC05F1 requiring predominance of eclogite in the source (Fig. 3.7). Thus, this model may provide significant constraints on the origin/source of carbonatites worldwide, irrespective of post-emplacement history. However, the nature of Re–Os systematics of magnetite-rich carbonatite IC11A having an extremely high Re content, paralleled by high γOs of +6,052 and Pt below the detection limit (Tab 3.2), remains enigmatic.

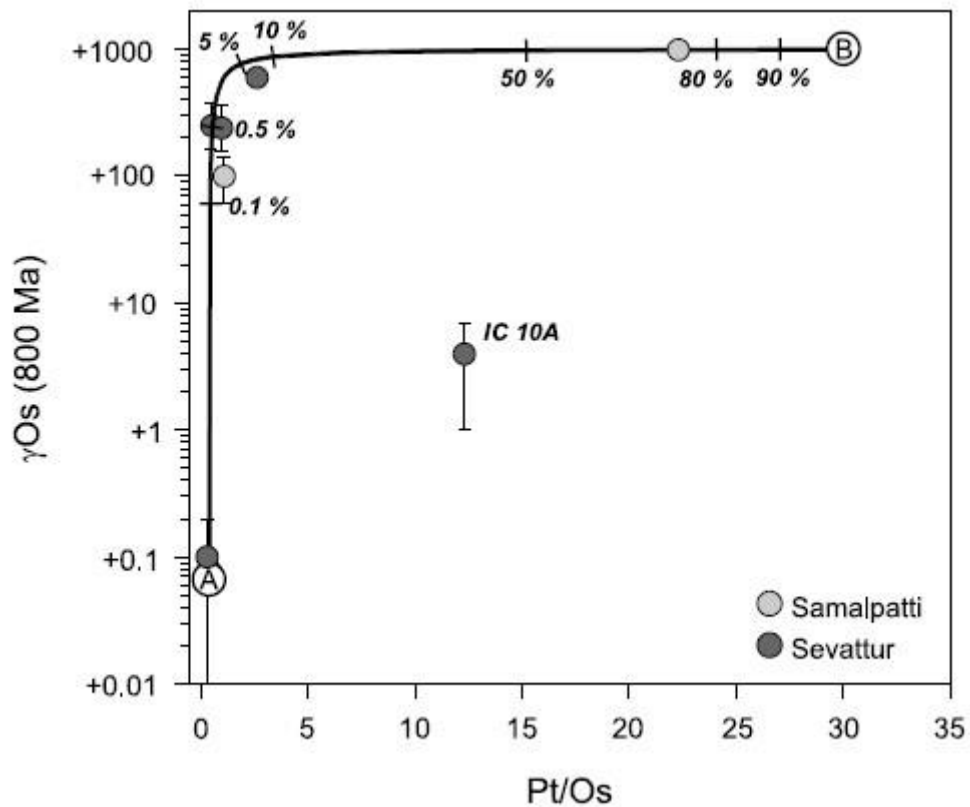


Fig. 3.7. Binary mixing model of γOs at 800 Ma versus Pt/Os for the Tamil Nadu carbonatites. Calculations show that to explain all samples but IC10A, variable mixing of two different sources must be considered – depleted mantle peridotite [A] with $\gamma\text{Os} = 0$, $\text{Pt}/\text{Os} = 0.4$ and recycled crust represented here by a hypothetical eclogite [B] with $\gamma\text{Os} = \sim 1000$, $\text{Pt}/\text{Os} = \sim 30$.

See main text for more details. The combined uncertainties are represented by 2σ values, but note that some of them are smaller than the symbol size.

3.5.3. Constraints on the origin of Mg–Cr-rich silicocarbonatites using HSE systematics

The unusual, volumetrically rare Mg–Cr-rich silicocarbonatites from Samalpatti occur as centimeter to decimeter-sized enclaves enclosed in pyroxenites with sharp contacts at hand specimen scale; they have been interpreted to originate through the melt immiscibility after the reaction of mantle-derived alkali-CO₂-rich melts and pyroxenites (Ackerman et al., 2017). Alternatively, Krátký et al. (2018) interpreted these rocks to originate through the carbonatite metasomatism of mantle peridotite precursors.

It is clear from the new data that these rocks contain strikingly higher HSE contents than calciocarbonatites, in spite of their very low S contents (<0.03 wt.%; Tab 3.2), and exhibit distinctive primitive mantle-normalized patterns (Fig. 3.3). The high I-PGE contents, paralleled by variable but mostly only slightly radiogenic initial $^{187}\text{Os}/^{188}\text{Os}$ ratios, agree with direct incorporation of enriched mantle-derived material into parental melts diagnosed by increased concentrations of Cr (up to 1,800 ppm) and Ni (up to 200 ppm) as well as a well-defined positive correlation between Os and Ni (not shown). On the other hand, variable incorporation of crustal material is evidenced by highly positive $\gamma\text{Os}_{800\text{Ma}}$ values of +190 and +370, found for samples IC03D and IC06E, respectively, and negative correlation between Os and K₂O concentrations (Fig. 3.8). The intimate relationship of Mg–Cr-rich silicocarbonatites with host pyroxenites can be easily recognized by almost identical HSE patterns (Fig. 3.3b–c) and Re–Os isotopic composition of pyroxenite IC07D matching with those of Mg–Cr-rich silicocarbonatites (Fig. 3.5). In contrast, the strongly fenitized pyroxenite IC06D exhibits crustal-like HSE signature and γOs (+1,780; Fig. 3.5) attesting to a strong crustal overprint. Collectively, the HSE composition of peculiar Mg–Cr-rich silicocarbonatites can be best explained by mixing of melts derived from an enriched mantle with pyroxenites which previously suffered intense fenitization by K₂O-dominated fluids which had escaped from carbonatite magmas (cf. Subramanian et al., 1978; Viladkar and Subramanian, 1995). While both investigated pyroxenites lie at the end of the Mg–Cr-rich silicocarbonatite composition in the [Os] vs. γOs space, their major/trace element and Sr–Nd–Pb isotopic compositions (Ackerman et al., 2017) suggest that they do not represent an end member in this scenario. Positive co-variations between Pt, Pd, and Re (Fig. 3.8) indicate that these three elements behave coherently and the well-developed positive correlation between Pt and MgO (Fig. 3.8) altogether argue for a source coming predominantly from the upper mantle. The nature of high Pt enrichment found in the Mg–Cr-rich carbonatites (Fig. 3.3b) remains unknown, but considering low sulfur contents, we may speculate that at least Pt is likely bound to some yet unrecognized Fe-, Te- or As-bearing platinum-group mineral phase (e.g., Lorand and Luguët, 2016) in these samples.

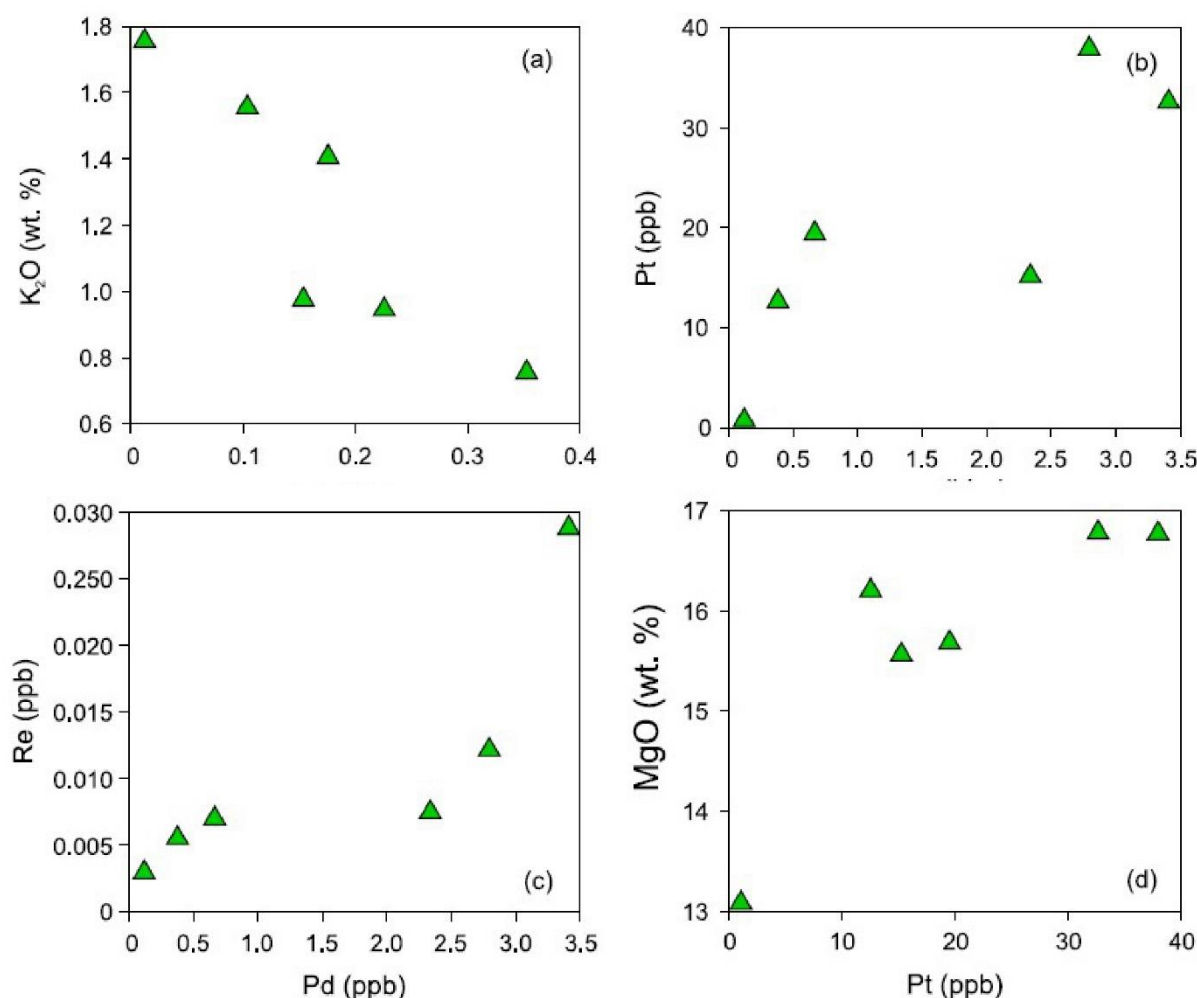


Fig. 3.8. Plots of co-variations of Os, Pt, Re, K₂O, and MgO concentrations for the Tamil Nadu Mg–Cr-rich silicocarbonatites. Note the excellent negative correlation found for K₂O versus Os (a) and positive correlations between Pt and Re versus Pd (b, c) as well as Pt versus MgO (d).

3.5.4. Nature and sources of silicate alkaline rocks and their relationship to carbonatites

The monzogabbros and a syenite from this study show a wide range of overlapping (and low) HSE concentrations with no clear relationship to sulfur contents (Fig. 3.2). These samples exhibit primitive mantle-normalized patterns showing mostly progressive enrichments from Os to Re (Fig. 3.3) and, in particular, highly radio-genic initial $^{187}\text{Os}/^{188}\text{Os}$ ratios (γ_{Os800Ma} from +356 to +3,494; Tab 3.2). Detailed petrography, underscored by sulfur determinations, revealed a presence of common late-stage pyrite mineralization at Samalpatti and Sevattur, but these samples were excluded from the dataset as their Re–Os systematics was clearly perturbed by this process (e.g., Re in excess due to formation of secondary pyrite). Thus, the highly radiogenic Os isotopic compositions of monzogabbros and a syenite argue for their derivation from crustal lithologies with no or only negligible mantle material

contribution, in agreement with their Sr–Nd–Pb isotopic systematics (Ackerman et al., 2017). Lower γOs values found for Samalpatti versus Sevattur samples (Tab 3.2, Fig. 3.5a) call for a more juvenile nature of the melts for Samalpatti. Nevertheless, it is clear that the source of these silicate alkaline rocks was entirely different from that envisaged for carbonatites, which is in agreement with previous assumptions that at least carbonatite magmas from Samalpatti represent the latest evolutionary stage of the area (Subramanian et al., 1978; Viladkar and Subramanian, 1995).

3.6. Conclusions

The first comprehensive dataset on the combined HSE abundances and Re–Os isotopic compositions are reported for a well-characterized suite of carbonatites and associated silicate rocks from south India with the aim to unravel their sources and histories, and to place first-order HSE constraints on effects of ubiquitous carbonatite metasomatism in the Earth’s mantle. The new data shows a range of HSE abundances with only a limited compositional overlap to MORB and with predominantly low HSE bud-get in calciocarbonatites ($\Sigma\text{HSE} < 1.2$ ppb), most likely reflecting sulfide retention in the source. Combined $^{187}\text{Re}/^{188}\text{Os}$ ratios (0.10–217), $^{187}\text{Os}/^{188}\text{Os}$ ratios (0.186–10.4), and initial γOs values back-calculated to 800 Ma (from +0.1 to +6,052) predict that most Tamil Nadu calciocarbonatites were plausibly derived from a carbonated peridotite source with <10% recycled component. The general model would thus provide significant constraints on the origin/source of carbonatites, irrespective of their post-emplacement history. Elevated HSE abundances ($\Sigma\text{HSE} = 14\text{--}41$ ppb) have been found in unusual, volumetrically minor, Mg–Cr-rich silicocarbonatites, with HSE patterns almost identical to those of host pyroxenites, including high Pt enrichment source of which remains yet unknown. Three out of five Mg–Cr-rich silicocarbonatites yield a narrow range of super-chondritic $^{187}\text{Os}/^{188}\text{Os}$ values from 0.145 to 0.183 resulting in $\gamma\text{Os}_{800\text{Ma}}$ values between +18 and +48, while two other Mg–Cr-rich silicocarbonatites exhibit more radiogenic compositions, providing evidence of extensive fenitization. This points to post-emplacement processes which may add to the complexity of carbonatite evolution. Associated silicate lithologies (pyroxenites, monzogabbros, syenite) mostly have low HSE contents ($\Sigma\text{HSE} < 2.3$ ppb), and highly radiogenic Os iso-topic compositions of these rocks argue for their derivation from crustal lithologies with no or only negligible contribution of mantle material. Considering the overall low HSE abundances, we posit that carbonatite magmas are less feasible to modify global HSE budgets in Earth’s mantle even in the case of large-scale carbonatite metasomatism. Contrary to this, extremely radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values found in some Tamil Nadu carbonatites can produce significant modification to the Re–Os isotopic composition of mantle peridotites during carbonatite melt percolation at high melt/rock ratios. We stress, however, that further tuning of such models requires additional new combined data on HSE abundances and Re–Os isotopic systematics in carbonatites and associated host rocks from a broader range of settings.

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Chapter 4

Significance of highly siderophile element and Re–Os isotope systematics in global carbonatites

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Abstract

The systematics of highly siderophile elements (HSE) in carbonatites have rarely been investigated although carbonatite melts are among key metasomatic agents in the Earth's mantle. Thus, establishing the Os isotope systematics of carbonatites is of prime importance because carbonatite metasomatism might play a determining role in driving $^{187}\text{Os}/^{188}\text{Os}$ signature of the Earth's mantle as a consequence of extreme mobility of carbonatite liquids. In this study, a suite of carbonatites from continental settings was analyzed for HSE abundances and Re–Os isotope systematics, combined with detailed

petrography of sulfide phases, to provide constraints on the HSE behavior during the formation of carbonatite melts, the role of sulfides in the distribution of HSE and the reliability of Re–Os isotope compositions. All investigated carbonatites display low $\Sigma\text{HSE} < 1$ ppb whereby calciocarbonatites exhibit supra-chondritic $\text{Os}_\text{N}/\text{Ir}_\text{N}$ ratios from ~ 1.4 to 15, in contrast to magnesiocarbonatites and Mg/Fe-rich carbonatites showing exclusively sub-chondritic $\text{Os}_\text{N}/\text{Ir}_\text{N}$. We posit that the preferential removal of Os over Ir during the segregation of calcite-normative melts from the co-existing S-rich silicate melts is the main driver of Os/Ir elemental fractionation. The present-day $^{187}\text{Os}/^{188}\text{Os}$ ratios in carbonatites range from mildly unradiogenic (~ 0.124) to extremely radiogenic values (~ 115 – 152), paralleled by highly variable $^{187}\text{Re}/^{188}\text{Os}$ ratios ranging from 0.096 to $\sim 26,000$, and without any clear relationship to the carbonatite type or emplacement age. The Re–Os systematics of carbonatites appear to be significantly modified by hydrothermal processes resulting in either removal of both Re and Os, or Re addition and consequently commonly negative calculated γOs values attesting to a rather limited potential of the Re–Os systematics to evaluate the nature of carbonatite melts. Conversely, limited Re–Os data for the samples that reflect primary signatures indicate the largely radiogenic $^{187}\text{Os}/^{188}\text{Os}$ nature of carbonatite melts. Nevertheless, carbonatite melts may, in part, be responsible for the radiogenic γOs values commonly observed in mantle-derived silicate melts influenced by carbonatite-like metasomatism.

Keywords: Carbonatite, Highly siderophile elements, Re-Os isotopes, IPGE, Mantle

4.1. Introduction

Mantle-derived melts provide important clues on the nature and temporal evolution of their mantle sources (Walzer and Hendel, 2022). While the essential information mainly comes from basaltic melts that formed through partial melting of peridotites, a number of low-degree partial melts (e.g., alkaline basalts, kimberlites, lamproites) highlight the importance of other lithologies (pyroxenites, eclogites) and volatiles ultimately contributing to the processes of crustal formation, which is critical to our understanding of silicate Earth (Hofmann, 1997; White and Hofmann, 1982).

Carbonatite melts represent a remarkable type of magma due to their extremely low viscosity (e.g., Kono et al., 2014; Treiman and Schedl, 1983) and relatively low solidus temperatures (Bell and Titon, 2002). Petrogenetic models of carbonatite melt formations, i.e., melting of CO₂-rich mantle lithologies, progressive evolution of carbonate-rich silicate melts through either liquid immiscibility or extreme degree of fractional crystallization (e.g., Lee and Wyllie, 1998; Weidendorfer et al., 2017) remain under-constrained because about 74% of known carbonatites are associated with alkaline silicate rocks which are considered to testify to their non-primary mantle origin (Yaxley et al., 2021). Carbonatites are present in all lithospheric settings (continental and oceanic) and their origin appears to be related to major melt-forming events such as crustal extension with or without plume-related activity (Woolley and Kjarsgaard, 2008a). Nevertheless, the formation of carbonatite melts is limited to suitable P–T–X–fO₂ conditions (Yaxley et al., 2019). Depending on their MgO–CaO–FeO_T proportions, common intrusive carbonatites can be classified as calciocarbonatites, magnesiocarbonatites, and Fe-rich/ferrocarbonatites (note that ferrocarbonatites *sensu stricto* require the presence of ankerite or siderite), while the eruptive carbonatites are more commonly represented by residual melts (Guzmics et al., 2019; Vasyukova et al., 2023; Weidendorfer et al., 2017), as in the case of the sole known active carbonatite volcano at Oldoinyo Lengai, Tanzania (Peterson, 1990), although pristine eruptive calciocarbonatites may also occur (Rappich et al., 2024).

Highly siderophile element (HSE – Os, Ir, Ru, Pd, Pt) geochemistry, combined with Re–Os isotope systematics, represents a powerful tool to decipher the mantle sources and evolution of mantle-derived melts. Until now, surveys of HSE systematics have predominantly been focused on basaltic and/or komatiitic lithologies (e.g., Day, 2013) while studies on CO₂-rich silicate rocks (lamproites, kimberlites; e.g., Krmíček et al., 2020; Maier et al., 2017) or even carbonatites (Ackerman et al., 2019) are limited. This shortage of detailed investigations of HSE systematics of carbonatites is significant considering that carbonatites can serve as an efficient transfer agent of sulfur and HSE in the Earth's mantle and that carbonatite metasomatism may have a significant impact on its HSE systematics (e.g., Chowdhury et al., 2021; Coltorti et al., 1999; Liu et al., 2015; Rudnick et al., 1993). Therefore, detailed HSE data for various types of carbonatites is needed to understand possible mechanisms that control the HSE systematics of carbonatite melts. Here, we present a comprehensive HSE dataset for

selected carbonatite bodies from different settings, paralleled by detailed petrography of possible HSE carriers. We discuss the elemental and isotope signatures of carbonatites with respect to possible HSE carriers and the significance of I–PGE fractionation characteristic for calciocarbonatites.

4.2. Studied carbonatites and overview of their geological settings

In total, 30 carbonatite samples from 10 locations (Fig. 4.1) in continental settings (intraplate, LIPs), with emplacement ages from ~2060 to <40 Ma (Tab 4.1), were analyzed for HSE concentrations and Re–Os isotope compositions. These new data are supplemented with five additional samples from the Sevattur carbonatite body analyzed previously (Ackerman et al., 2019). Altogether, a comprehensive dataset of 33 carbonatite samples is used for further interpretations. Among these, 17 samples of calciocarbonatites, eight magnesiocarbonatites, five ferruginous calciocarbonatites including peculiar hematite-rich samples from the Fen Complex, Norway (so-called rödberg), and three silica-rich carbonatites were analyzed. The majority of the samples have <8 wt. % SiO₂, but some samples, namely calciocarbonatite sample AC03D (14 wt.% SiO₂) and silicocarbonatites have variably elevated SiO₂ contents of up to 22 wt. %, reflective of varying proportions of primary silicate phases (e.g., mica, pyroxene, olivine, feldspar) as a consequence of liquid immiscibility from parental carbonated silicate melts (Ackerman et al., 2021). Three samples of silicified calciocarbonatites characterized by post-magmatic hydrothermal alteration by Si-rich fluids were also analyzed to investigate possible effects of silicification on the HSE systematics. Detailed geological descriptions for all investigated localities are given elsewhere and we only briefly summarize the salient features and characteristics of the occurrences below.



Fig. 4.1. Sketch map showing the occurrences of investigated carbonatite occurrences.

The Phalaborwa (South Africa) calcio-, Mg-rich-, and ferruginous carbonatites (~2060 Ma; Wu et al., 2011) are part of a compositionally zoned ultramafic–alkaline complex intrusive into the Archean Kaapvaal Craton. With respect to their Sr–Nd–Hf isotope compositions, the carbonatites are considered to derive either from metasomatized mantle or mantle with a significant proportion of recycled crustal material (Eriksson, 1984; Wu et al., 2011; Yuhara et al., 2005). Two carbonatite generations occur, with the older one being genetically associated with phoscorite (Mg-silicate, apatite, and Fe-oxide rock; Giebel et al., 2019). In addition, the rocks experienced complex late and post-magmatic hydrothermal overprint (Giebel et al., 2017).

The Newania magnesiocarbonatite (~1470 Ma; Ray et al., 2013) intruded into the ~2.95 Ga Aravalli craton in NW India, and combined petrography, mineralogy, and radiogenic and stable (C–O–Sr–Nd–Pb) isotope systematics argue for derivation of the carbonatite melt from the subcontinental lithospheric mantle source, later enriched in LREE by carbonate-rich fluids/melts (Banerjee et al., 2021; Doroshkevich et al., 2010; Ray et al., 2013).

The Neoproterozoic Sevattur carbonatite complex in Tamil Nadu (southern India) hosts numerous calciocarbonatite and magnesiocarbonatite dykes emplaced in a syenite body (~801 Ma; Schleicher et al., 1997). They were likely derived from an enriched mantle source with negligible modification of parental melts *en route* to the surface which is different from significant remobilization and recrystallization noticed for the neighboring Samalpatti complex (Ackerman et al., 2017).

The Fen carbonatite complex (FCC; Norway) intruded into the western margin of the Oslo Rift at ~583 Ma (Meert et al., 1998). The predominant calciocarbonatites are accompanied by minor magnesio- and ferruginous carbonatites, collectively derived from the depleted upper mantle while they also were significantly contaminated by crustal material (Andersen, 1987). Primary Fe-carbonates in the ferruginous carbonatites are hydrothermally altered to hematite forming the hematite–calcite–dolomite mineral association (so-called “rödberg”) with notably elevated Th and REE contents (Marien et al., 2018).

The Lemitar Mts. carbonatites (~450 Ma; New Mexico, USA) intruded into Precambrian rocks (McLemore, 1987) as a dike swarm and, together with the Iron Hill carbonatites (~565 Ma, Colorado, USA; Van Allen et al., 1986 and references therein), they are related to Ediacaran–Ordovician magmatism. The Lemitar Mts. carbonatites underwent partial hydrothermal alteration (McLemore, 1987), apparent in recrystallized REE minerals phases. Carbonatites at both localities commonly have elevated SiO₂ contents (up to 22 wt.%) and their origin appears to be associated with liquid immiscibility (Ackerman et al., 2021).

The Sung Valley calciocarbonatite intruded into the Proterozoic bedrock at ca. 107 Ma (Ray et al., 1999). Srivastava and Sinha, 2005 suggested that these carbonatites represent low-degree melts

from a the metasomatized mantle source, probably caused by the impingement of the Kerguelen mantle plume (Veena et al., 1998).

Calciocarbonatites from Amba Dongar, NW India (~65 Ma; Ray and Pande, 1999) are related to the Réunion mantle plume active during the formation of the Deccan Trap basalts (Bell et al., 1998; Chandra et al., 2017; Simonetti et al., 1995). Chandra et al., 2019 proposed carbonatite formation via liquid immiscibility from a carbonated silicate magma derived through low-degree partial melting of CO₂-rich subcontinental lithospheric mantle contaminated by local Archean gneisses.

The East African Rift System (EARS) hosts the world's youngest carbonatites. The studied Ol Doinyo Dili carbonatite body (calcio- and magnesiocarbonatite) is linked with magmatism of the Tanzanian craton at around 100–120 Ma (Dawson, 1997) while the twinned Tororo–Sukulu carbonatite complex (Uganda) appears to be <40 Ma in age (Ernst and Bell, 2010). The Tororo and Sukulu calciocarbonatites are thought to have been derived via a liquid immiscibility process from parental CO₂-rich silicate melts (Ackerman et al., 2021; Benkó et al., 2021).

Table 1 HSE concentrations and Re-Os isotopic compositions of carbonatites from this study.

Sample	BCBnoS1	BCBws5	TCBno5	TCBws3	TCBws1	TCBws2	NE9	NE19	IC16A	IC16B	IC10J	IC10J_DUP
Locality	Phalaborwa	Phalaborwa	Phalaborwa	Phalaborwa	Phalaborwa	Phalaborwa	Newania, India	Newania, India	Sevattur	Sevattur	Sevattur	Sevattur
Rock	Ca-carbonatite	Ca-carbonatite	Ca-carbonatite	Ferruginous carbonatite	Ferruginous carbonatite	Mg-rich carbonatite	Mg-carbonatite	Mg-carbonatite	Ca-carbonatite	Ca-carbonatite	Ca-carbonatite	Ca-carbonatite
Age (Ma)	2060 ± 1 ^a	2060 ± 1 ^a	2060 ± 1 ^a	2060 ± 1 ^a	2060 ± 1 ^a	2060 ± 1 ^a	1473 ± 63 ^b	1473 ± 63 ^b	801 ± 11 ^c	801 ± 11 ^c	801 ± 11 ^c	801 ± 11 ^c
S (wt. %)	0.023	0.746	bdl	1.407	2.176	1.57	bdl	0.01	bdl	0.035	0.017	0.017
Re (ppb)	0.003	0.012	0.020	0.027	0.023	0.006	0.203	0.062	0.002	0.011	0.057	0.068
2σ	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001
Os	0.001	0.001	0.002	0.005	0.003	0.002	0.050	0.026	0.121	0.243	0.193	0.097
2σ	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0004	0.0002	0.0009	0.0007	0.0017	0.0007
Ir	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.012	0.011
Ru	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.004	0.002
Pt	0.013	0.017	0.013	0.292	0.101	bdl	bdl	bdl	0.122	0.069	0.103	0.249
Pd	bdl	0.128	bdl	0.601	0.195	0.054	bdl	0.071	0.258	0.240	0.495	0.560
¹⁸⁷ Re/ ¹⁸⁸ Os	11.5	40.4	55.8	26.1	33.4	13.5	30.6	13.6	0.096	0.223	1.47	3.71
2σ	4.1	6.5	7.1	1.4	2.5	2.6	0.3	0.3	0.033	0.020	0.03	0.07
¹⁸⁷ Os/ ¹⁸⁸ Os	0.32	0.37	n.d.	0.209	0.532	0.56	4.47	1.725	0.411	0.124	0.448	0.904
2σ	0.19	0.17	n.d.	0.048	0.080	0.13	0.04	0.020	0.018	0.002	0.023	0.017
¹⁸⁷ Os/ ¹⁸⁸ Os (i)	negative	negative	negative	negative	negative	0.088	3.71	1.39	0.410	0.121	0.428	0.854
γ _{Os}	negative	negative	negative	negative	negative	negative	3070	1090	240	-1	250	600
2σ	n.c.	n.c.	n.c.	n.c.	n.d.	n.d.	410	170	80	n.c.	90	120

Table 1 continue

Sample	IC10A	CFN 3	CFN 3 DUP	CFN 7	CFN 9	CFN 9 DUP	UC17A	UC17B	UC02	UC03A	UC04	UC07A
Locality	Sevattur	Fen Carbonatite Complex	Fen Carbonatite Complex	Fen Carbonatite Complex	Fen Carbonatite Complex	Fen Carbonatite Complex	Iron Hill	Iron Hill	Lemitar Mts.	Lemitar Mts.	Lemitar Mts.	Lemitar Mts.
Rock	Ca- carbonatite	Ca- carbonatite	Ca- carbonatite	Rödberg	Mg- carbonatite	Mg- carbonatite	Ferruginous carbonatite	Fe-rich silicocarbon- atite	silicified carbonatite	silicified carbonatite	Mg carbonatite	Mg carbonatite
Age (Ma)	801 ± 11 ^c	583 ± 15 ^d	583 ± 15 ^d	583 ± 15 ^d	583 ± 15 ^d	583 ± 15 ^d	565 ^c	565 ^c	515 ^f	515 ^f	515 ^f	515 ^f
S (wt. %)	0.015	0.28	0.28	2.150	0.15	0.15	bdl	0.705	0.282	bdl	bdl	0.24
Re (ppb)	0.015	0.426	0.544	0.008	14.1	11	0.076	0.286	1.31	0.622	4.2	1.101
2σ	0.001	0.004	0.005	0.001	0.152	0.115	0.001	0.001	0.007	0.002	0.007	0.002
Os	0.016	0.008	0.001	0.011	0.042	0.042	0.001	0.011	0.031	0.033	bdl	bdl
2σ	0.0001	0.0001	0.0001	0.0001	0.0019	0.0015	0.0001	0.0002	0.0011	0.0004	bdl	bdl
Ir	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.258	bdl	bdl	0.016	bdl
Ru	0.006	bdl	bdl	0.012	bdl	bdl	bdl	0.049	bdl	bdl	0.039	bdl
Pt	0.197	bdl	bdl	0.019	bdl	bdl	0.501	1.271	0.234	0.213	0.350	0.156
Pd	0.134	bdl	bdl	0.025	bdl	bdl	bdl	3.648	0.064	0.052	0.101	0.040
¹⁸⁷ Re/ ¹⁸⁸ Os	4.44	269	3050	4.37	25600	25300	473	142	849	119	n.d.	n.d.
2σ	0.16	4.3	470	0.27	1560	1300	84	5	29	1.9	n.d.	n.d.
¹⁸⁷ Os/ ¹⁸⁸ Os	0.186	0.587	5.22	1.183	115	152	0.296	1.068	23.9	2.5442	n.d.	n.d.
2σ	0.008	0.035	0.84	0.023	8	8	0.156	0.059	1.2	0.0652	n.d.	n.d.
¹⁸⁷ Os/ ¹⁸⁸ Os (i)	0.127	negative	negative	1.141	negative	negative	negative	negative	17	1.5205	n.d.	n.d.
γ _{Os}	4	negative	negative	830	negative	negative	negative	negative	13300	1130	n.d.	n.d.
2σ	3	n.c.	n.c.	145	n.c.	n.c.	n.c.	n.c.	1760	230	n.c.	n.c.

Table 1 continue

Sample	UC09	SUNG9	IC41A	17AM5	IC42	IC41B	IC40	AC05B	AC05C	AC01G	AC03D
Locality	Lemitar Mts.	Sung Valley	Amba Dongar	Amba Dongar	Amba Dongar	Amba Dongar	Amba Dongar	Oldoinyo Dili	Oldoinyo Dili	Sukulu	Tororo
Rock	Mg- carbonatite	Ca- carbonatite	Ca- carbonatite	Ca- carbonatite	Ca- carbonatite	Ca- carbonatite	Ca- carbonatite	silicified carbonatite	Ca- carbonatite	Mg- carbonatite	Ca- carbonatite
Age (Ma)	515 ^f	107 ± 0.8 ^g	65 ± 0.8 ^h	65 ± 0.8 ^h	65 ± 0.8 ^h	65 ± 0.8 ^h	65 ± 0.8 ^h	100 ⁱ	100 ⁱ	40 ^j	40 ^j
S (wt. %)	0.35	bdl	0.04	bdl	0.02	bdl	0.09	0.015	bdl	bdl	0.023
Re (ppb)	8.083	0.025	0.150	1.486	0.198	0.443	0.035	0.061	0.272	0.687	0.582
2σ	0.007	0.001	0.001	0.014	0.001	0.003	0.001	0.001	0.001	0.005	0.004
Os	bdl	0.034	0.034	0.040	0.008	0.006	0.008	0.003	0.002	0.014	0.001
2σ	bdl	0.0002	0.0002	0.0003	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Ir	0.045	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Ru	0.087	bdl	bdl	bdl	bdl	bdl	bdl	0.013	bdl	bdl	0.031
Pt	0.348	bdl	0.113	0.021	0.075	0.957	0.388	0.007	bdl	0.038	0.009
Pd	0.268	bdl	0.046	bdl	0.087	bdl	0.030	0.156	bdl	bdl	bdl
¹⁸⁷ Re/ ¹⁸⁸ Os	n.d.	3.59	22.9	204	205	430	22.2	100	960	250	3100
2σ	n.d.	0.15	0.2	3	9	18	0.8	7	140	4	680
¹⁸⁷ Os/ ¹⁸⁸ Os	n.d.	0.128	0.784	1.097	5.81	2.32	0.917	1.31	1.47	0.89	2.03
2σ	n.d.	0.008	0.010	0.017	0.26	0.10	0.034	0.11	0.26	0.021	0.50
¹⁸⁷ Os/ ¹⁸⁸ Os (i)	n.d.	0.122	0.760	0.89	5.6	1.9	0.89	1.31	1.44	0.73	negative
γ _{Os}	n.d.	-4	500	610	4320	1360	610	930	1040	480	negative
2σ	n.c.	n.c.	86	110	620	280	140	260	380	110	n.c.

Tab. 4.1. HSE concentrations and Re-Os isotopic compositions of carbonatites from this study 2σ standard deviation; n.d. - not detected, n.c. - not calculated bdl. – below detection limits; γ_{Os} values calculated using chondrite composition of Shirey and Walker (1998); ¹⁸⁷Os/¹⁸⁸Os_{Schon} = 0.1297, ¹⁸⁷Re/¹⁸⁸Os_{Schon} = 0.40186; ^{a)} Wu et al., 2011, ^{b)} Ray et al., 2013, ^{c)} Schleicher et al., 1997, ^{d)} Meert et al., 1998, ^{e)} Olson et al., 1977, ^{f)} McLemore, 1982, ^{g)} Ray et al., 1999, ^{h)} Ray and Pande, 1999, ⁱ⁾ Dawson, 1997, ^{j)} Woolley and Kjarsgaard, 2008a.

4.3. Methods

An *Olympus BX51* Fluorescence Microscope equipped with a DP70 camera was used for preliminary optical examination of sulfide and oxide phases. Subsequent phase identification was carried out using a *Tescan Vega 3XMU* SEM housed at the Institute of Geology of the Czech Academy of Sciences (IG

CAS). The analyses were conducted with a probe current beam of 10nA and an accelerating voltage of 15kV.

The HSE concentrations and Re–Os isotope compositions were determined at IG CAS (chemistry and mass spectrometry) and Czech Geological Survey (mass spectrometry) following the protocol detailed in (Ackerman et al., 2019). In brief, 2–4 g of powdered sample was weighed into 60 ml Savillex Teflon beakers along with the appropriate amounts of ^{190}Os , ^{185}Re , and ^{99}Ru – ^{191}Ir – ^{105}Pd – ^{194}Pt spikes and decarbonized following the procedure of Xu et al. (2008b), using consecutive addition of 1 ml 1M HCl, 2 ml 4M HCl and finally 7 ml 14M HCl. Thereafter, the solutions were closed and left on a hotplate at 60°C for ~24 hours. Subsequently, the solutions were dried and the residues were dissolved in 9 ml of *reverse aqua regia* (5:4 v/v HNO_3/HCl), transferred into pre-cleaned and cooled Carius Tubes, sealed, and decomposed at 240 °C for 72 hours. Osmium was separated from the solution using CHCl_3 and HBr (Cohen and Waters, 1996), followed by purification using the micro-distillation technique (Birck et al., 1997). Rhenium, Ir, Ru, Pt, and Pd were isolated by anion-exchange chromatography using AG 1x8 (Eichrom) and their contents were measured using an *Element 2* ICPMS coupled with *Aridus II*, housed at IG CAS, with PGE and Re reference solutions used for mass bias corrections. Osmium isotope compositions and concentrations were determined at either IG CAS or Czech Geological Survey using a *Triton Plus* thermal ionization mass spectrometer operated in negative mode (N-TIMS; Creaser et al., 1991b; Völkening et al., 1991). The average total procedural blanks of the entire analytical protocol were as follows: Os = 0.6 ± 0.4 pg with $^{187}\text{Os}/^{188}\text{Os}$ of 0.143 ± 0.030 , Ir = 4.4 ± 2.4 pg, Ru = 16 ± 5 pg, Pt = 23 ± 9 pg, Pd = 45 ± 26 pg, Re = 1.4 ± 0.8 pg. Considering very high sample amounts (2 to 4 g) and detected blank variability during the sample processing, the calculated detection limits for the entire analytical protocol were ~0.5 ppt Os, ~3 ppt Ir, ~10 ppt Ru, ~10 ppt Pt, ~15 ppt Pd and ~1 ppt Re. The overall uncertainty calculations include uncertainties on the Re–Os spike calibration, blank correction, sample age, decay constant, and mass spectrometry analyses.

4.4. Results

4.4.1 Petrography of potential HSE-bearing phases

A detailed petrography focused on mineral phases capable to host elevated HSE contents (e.g., Fe–Cu–Ni sulfides, magnetite/hematite, Bi–Te–As phases; Alard et al., 2002; Aulbach et al., 2021) was carried out for all samples from this study, irrespective of their bulk HSE concentrations.

Apart from common magnetite characteristic especially for Fe-rich carbonatites, the Phalaborwa carbonatites contain variable proportions of Cu-sulfides such as chalcopyrite, bornite, and cubanite (Fig. 4.2.a,b) consistent with high bulk rock Cu contents, up to 1.4 wt. % (Supplementary

Tab 4.1). Both bornite and chalcopyrite occur as up to 0.5 mm large euhedral to anhedral grains, veinlets filling fractures in carbonate phases, or as lamellae. Chalcocite (Cu_2S) and covellite (CuS) are observed as alteration products of bornite. Other sulfides are minor pyrrhotite, galena, greigite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{S}_4$), and cobalto-pentlandite [$(\text{CoFeNi})_9\text{S}_8$]. Additionally, tellurium-bearing phases such as altaite (PbTe ; $\sim 2\text{--}4\text{ }\mu\text{m}$), and radhakrishnaite [$\text{PbTe}(\text{Cl},\text{S})_2$] were found while sperrylite (PtAs_2) noticed previously by Rudashevsky et al. (2004) was not confirmed by our study.

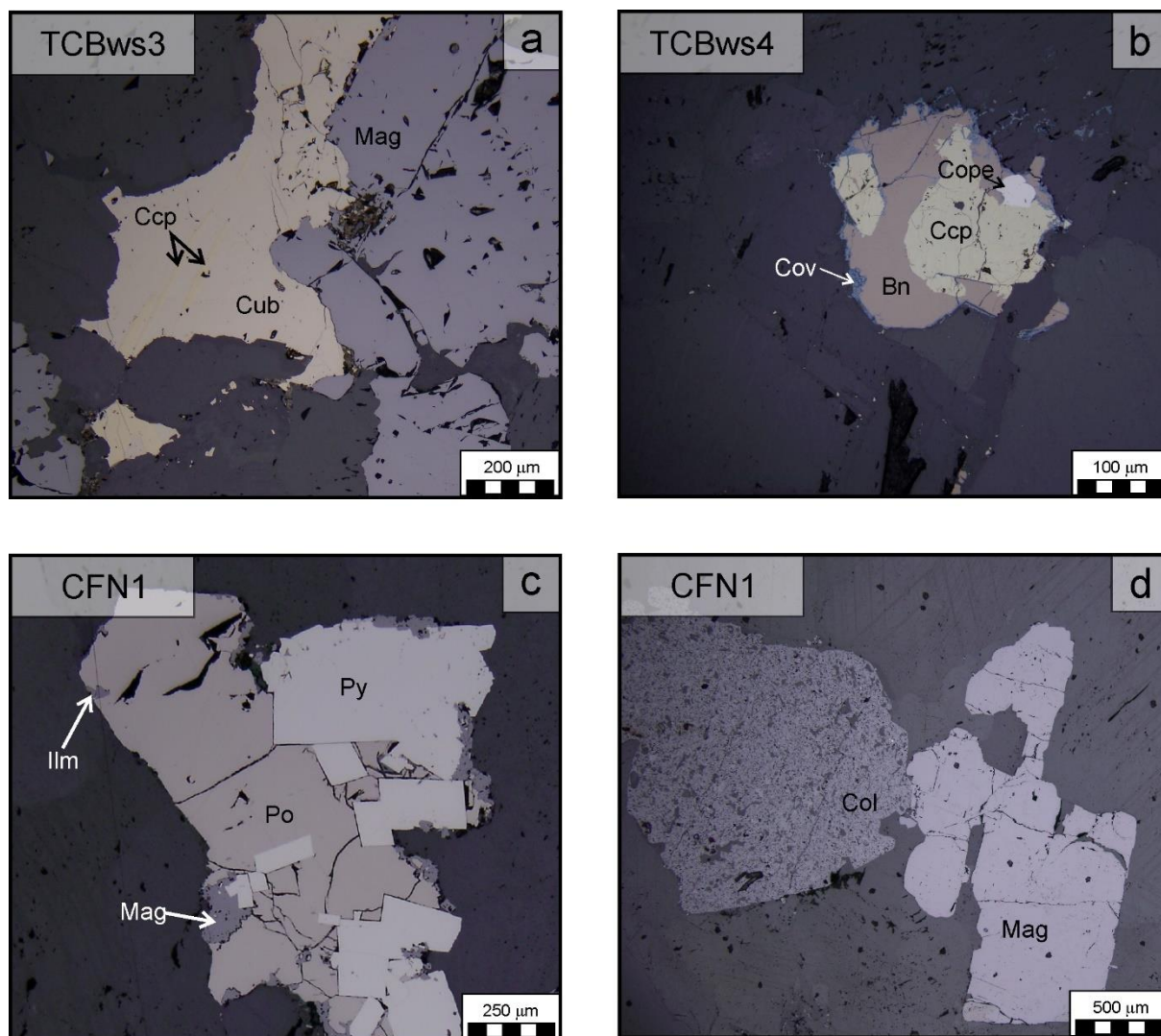


Fig. 4.2. BSE (back-scattered electron) images of (a, b) Phalaborwa ferruginous carbonatite and calciocarbonatite, respectively; and (c, d) Fen Carbonatite Complex calciocarbonatite. Bn – bornite, Ccp – chalcopyrite, Col - columbite (Fe), Cope - cobaltopentlandite, Cov - covellite, Cub - cubanite, Ilm - ilmenite, Mag – magnetite, Po - pyrrhotite, Py – pyrite.

The Newania and Sevattur carbonatites contain magnetite with grains up to $\sim 70\text{ }\mu\text{m}$ long, while rare sulfides are represented by pyrite and pyrrhotite. When present, they form small ($< 20\text{ }\mu\text{m}$) isolated and/or interstitial grains, consistent with previous observations (Ackerman et al., 2019; Doroshkevich et al., 2010).

The Fen Complex carbonatites commonly contain up to a few millimeters long grains of columbite (Fig. 4.2c,d) and large grains of magnetite and pyrite, often oxidized to hematite. This oxidation is most pronounced in the “rödberg” sample CFN 7 with ~17.5 wt. % Fe₂O₃ producing a notably red color of the rock (Supplementary Tab 4.1). Accessory phases such as galena and columbite were also observed in rödberg.

The Lemitar Mts. and the Iron Hill carbonatites have variable contents of magnetite, sometimes oxidized to hematite, with the highest modal content of magnetite found in Fe-rich silicocarbonatite UC17B. At both localities, pyrite is an abundant interstitial phase, but it commonly suffers from late-stage oxidation (Ackerman et al., 2021).

The carbonatite from the Sung Valley does not contain any sulfide phase and has only a small content of magnetite. Similarly, no sulfides were observed in the Amba Dongar carbonatites from this study, in agreement with very low total sulfur contents (Supplementary Tab 4.1) although galena and pyrite have occasionally been reported (Magna et al., 2020; Viladkar, 2018). In contrast, magnetite represents an abundant phase, yet with largely variable modal proportions among the studied samples.

The EARS calciocarbonatites (Sukulu, Tororo, Oldoinyo Dili) contain magnetite in variable modal proportions while sulfides are virtually absent with the exception of sample AC03D from Tororo containing abundant up to ~50 µm large pyrite grains that accompany magnetite.

4.4.2 Highly siderophile element concentrations

The HSE contents and Re–Os isotope compositions along with the calculated initial γ Os (deviation from the evolution line of the chondritic uniform reservoir; CHUR) values of carbonatites from this study are given in Tab 4.1. Overall, the I-PGE (Os, Ir, Ru) as well as P-PGE (Pt, Pd) contents are extremely low in all studied rocks (Σ PGE < 1 ppb except for sample UC17B) with most of Ir and Ru values below the detection limits (Tab 4.1). With the exception of the Lemitar Mts. carbonatites, Os contents show a considerable variation with values as high as 0.24 ppb found in Sevattur (Ackerman et al., 2019). The concentrations of Pd and Pt usually do not exceed 0.3 ppb except for several carbonatite samples from Phalaborwa and Sevattur (up to ~0.6 ppb Pd) and sample UC17B from the Iron Hill with anomalously high Pt and Pd concentration (1.27 and 3.65 ppb, respectively). In comparison to somewhat variable but generally low PGE abundances, rhenium contents are varying over nearly four orders of magnitude. While most Re contents are lower than 0.4 ppb (and as low as 0.003 ppb), the Lemitar Mts. carbonatites collectively exhibit a notable Re enrichment (1.1–8.1 ppb). An extreme Re content of ~14 ppb was detected in sample CFN9 from the Fen Complex (Tab 4.1). No clear relationships between individual HSE have been observed (Fig. 4.3).

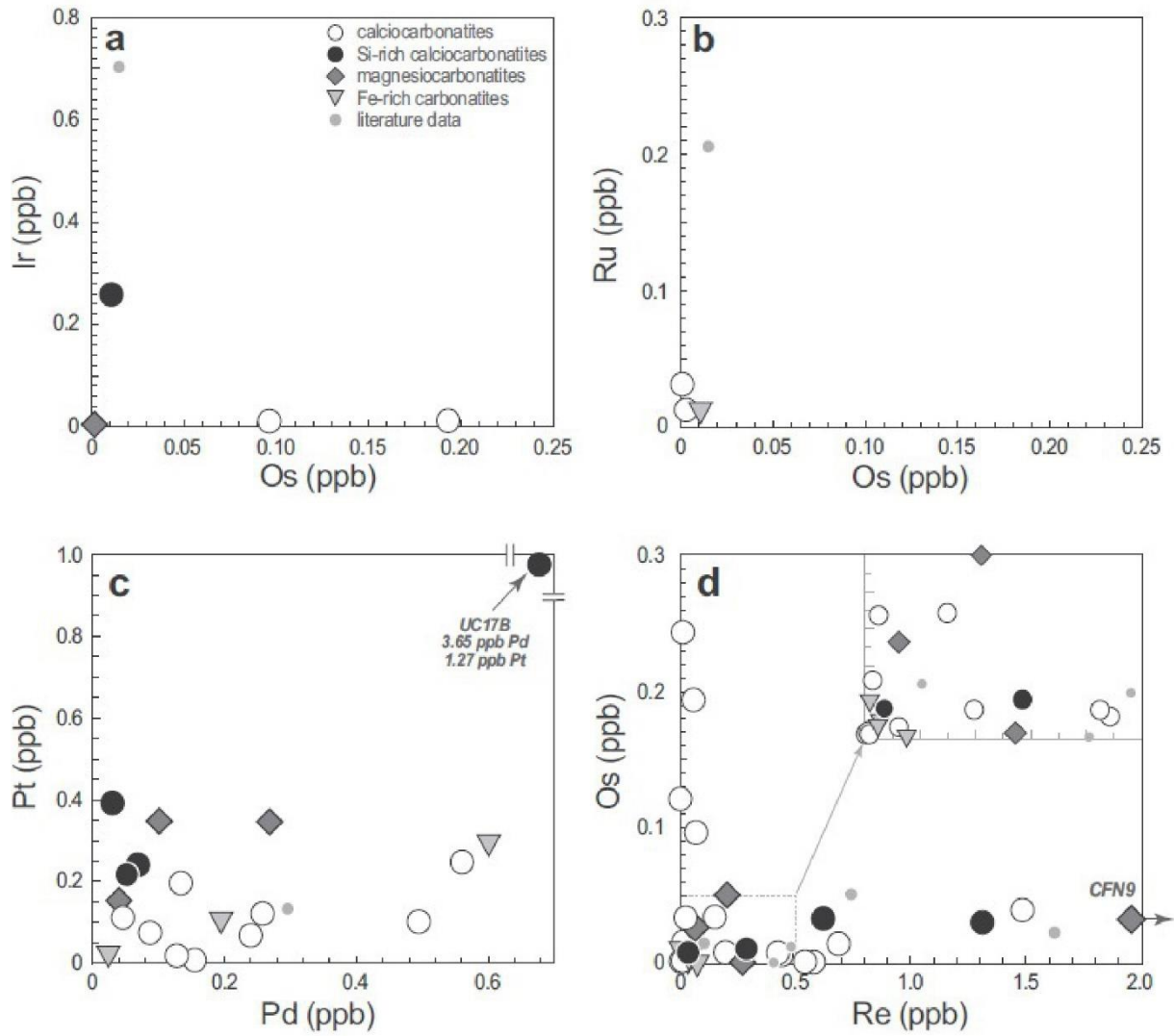


Fig 4.3. Binary plots of distribution of Os, Ir, Ru, Pt, Pd and Re. Note the absence of any inter-element correlations. Literature data are taken from Escrig et al. (2005), Pearson et al. (1995), Tappe et al. (2020b), and Widom et al. (1999).

The primitive mantle-normalized HSE patterns (Becker et al., 2006) of the studied carbonatites are plotted in Fig. 4.4. In spite of low HSE contents found for most samples, it appears that calciocarbonatites and silicified calciocarbonatites exhibit systematic enrichments of Os over Ir with Os_N/Ir_N ratios ranging from ~ 1.4 to 15 (hereafter termed **Type A**). Consequently, this results in a negative slope in primitive mantle-normalized I-PGE contents (Fig. 4.4). On the contrary, magnesiocarbonatites and Fe-rich carbonatites show an opposite trend of $Os_N/Ir_N < 1$ and a positive I-PGE slope (hereafter termed **Type B**). The Pt_N/Ir_N ratios vary from 4 to 114 in calciocarbonatites and silicified calciocarbonatites, with a mean value of 31 whereas Pt_N/Ir_N ratios in magnesiocarbonatites and Fe-rich carbonatites range from 7 to 159 with a mean value of 64. There are no clear correlations between individual HSE or ΣHSE versus CaO and other major elements contents which is in agreement with the observation of Ackerman et al. (2019) and Schweitzer (2019).

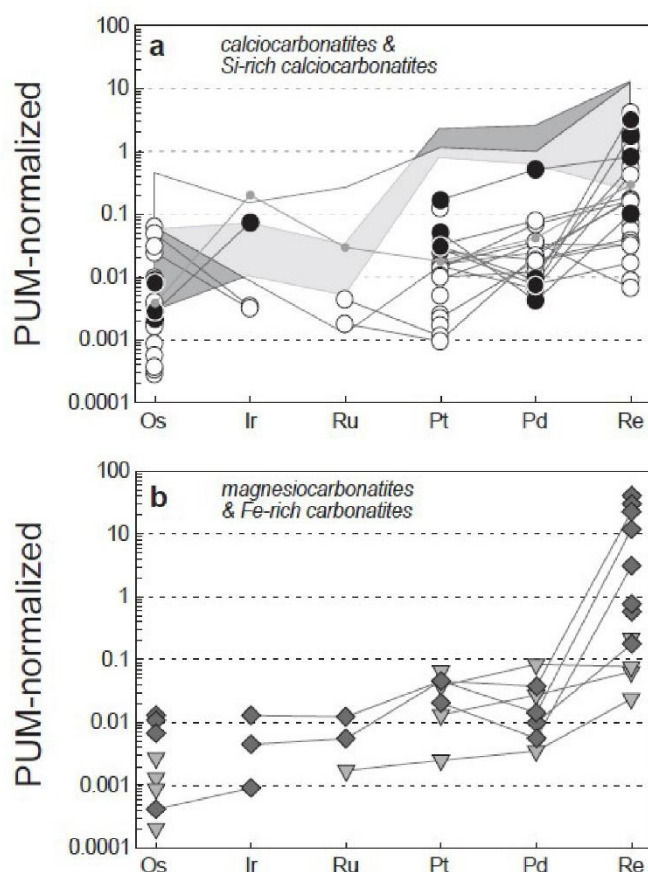


Fig. 4.4. Primitive upper mantle (PUM) normalized (Becker et al., 2006) highly siderophile element patterns of global carbonatites. Light grey field represents lamprophyres from the Yunnan Province (Gan and Huang, 2017) and Deccan basalts (Peters et al., 2017, 2016) with $Os_N/Ir_N > 1$ while the dark grey field corresponds to Emeishan flood basalts (Qi and Zhou, 2008).

4.4.3. Re–Os isotope compositions

The present-day $^{187}Os/^{188}Os$ isotope compositions of the studied rocks are extremely variable, ranging from mildly unradiogenic values (~ 0.124) to extremely radiogenic $^{187}Os/^{188}Os$ ratios (~ 115 – 152), which is also reflected in highly variable $^{187}Re/^{188}Os$ ratios ranging from 0.096 to $\sim 26,000$ (Tab 4.1). Consequently, the calculated initial γ_{Os} values for individual samples commonly result in highly negative values, suggesting significant post-emplacement modification of the Re–Os systematics, consistent with Re remobilization (section 4.5.1). Negative initial γ_{Os} values were calculated for ca. 50% of samples; all other samples with possibly reliable Re–Os compositions (see the calculated propagated errors in Tab 4.1) are characterized by largely positive and variable initial γ_{Os} values from +4 to +4,300 with no clear relationship to carbonatite type (supra-chondritic Os_N/Ir_N **Type A** or sub-chondritic Os_N/Ir_N **Type B**), age or major/trace element composition.

4.5. Discussion

4.5.1. Nature of possible HSE-bearing carriers in carbonatites and behavior of Re

Highly siderophile elements in mantle peridotites and their large-degree melts (e.g., komatiites, MgO-rich basalts) are predominantly bound to accessory mineral phases such as Fe–Ni–Cu sulfides (all HSE in variable proportions), high-temperature alloys and sulfides (I-PGE and Pt), arsenides (Pt) or tellurides (P-PGE) due to the large affinity of HSE to these phases (Lorand and Luguet, 2016; Waterton et al., 2021). In contrast, there is a fairly limited knowledge about possible HSE-bearing carriers in low-degree mantle-derived alkaline silicate melts or even carbonatites. When elevated HSE

contents are occasionally found in kimberlites or basalts, they typically are explained by entrapment of mantle xenoliths (e.g., Arslan et al., 2022; Maier et al., 2017).

With the exception of Phalaborwa carbonatites containing significant Cu mineralization, our study documents that carbonatites are characterized by variable but generally low sulfur contents (< 1 wt. %), in agreement with rather rare sulfide phases identified during petrographic investigation (see above). In the case of Phalaborwa, while the Cu sulfides are modally abundant, collectively very low bulk-rock Σ HSE contents ≤ 0.93 ppb indicate that Cu sulfides are of subordinate importance to the HSE budget and element systematics, in agreement with previous studies (e.g., Mansur et al., 2020). Overall, the absence of a relationship between total sulfur or base metals such as Ni, Co, or Cu and Σ HSE contents suggests that HSE in carbonatites are hosted by heterogeneously distributed accessory mineral phases, in agreement with the large variability in HSE contents within individual samples, as revealed on the basis of duplicate analyses (Tab 4.1 and Ackerman et al., 2019). Extremely low PGE concentrations prevent placing further constraints on the possible carrier phases, but some inferences can be made for Re, as it largely controls the Re–Os systematics and is thus most critical for the reliability of Re–Os isotope data.

While most of the studied samples have Re contents lower than 0.5 ppb, a number of samples from the Fen Complex and the Lemitar Mts. contain >1 ppb Re (Tab 4.1), significantly above what has so far been reported for the majority of mantle-derived melts (e.g., Gannoun et al., 2016 and references therein). This indicates Re enrichment associated with precipitation of a phase capable to accommodate Re to a large extent. In this respect, molybdenite (MoS_2) can contain up to several thousand ppm Re (Fleischer, 1959) because Re^{4+} has similar properties as Mo^{4+} . For example, Stein et al., 1997 found ~ 280 ppm Re in molybdenite from the Huanglongpu district, China, representing a rare Mo-rich carbonatite deposit (Song et al., 2016). Molybdenite represents a generally overlooked accessory phase in carbonatites, yet it has been identified both in the Lemitar Mts. (McLemore, 1987) and Fen Complex carbonatites (Grenne et al., 1999). Considering that samples from these two localities yield the highest Re contents compared to all other analyzed samples, we conclude that Re systematics in carbonatites may be largely controlled by the variable presence/appearance of molybdenite. This agrees with growing evidence for significant Mo enrichment in some carbonatites (e.g., Gaspers et al., 2020; Zheng et al., 2020) due to the preferential partitioning of Mo into carbonatite liquids (Jones et al., 1995).

4.5.2. Processes controlling concentrations of platinum-group elements in carbonatite melts and implications for their petrogenesis

If studies related to PGE (Os, Ir, Ru, Pt, Pd) mineralization in ultramafic–alkaline–carbonatite complexes (Fontana, 2006; Sazonov et al., 2021) and limited Re–Os data (see below) are omitted, the available datasets obtained for carbonatites so far includes only incomplete PGE data (Ir, Ru, Pd, Pt) reported for several carbonatites from China (Xu et al., 2008b) and the HSE dataset for the ~800 Ma Tamil Nadu carbonatites from Southern India (Ackerman et al., 2019). Collectively, both studies document that intraplate carbonatites exhibit variable but very low PGE concentrations generally similar to those reported for MORB-like and lamproite magmas (e.g., Bézous et al., 2005; Dale et al., 2008; Gannoun et al., 2016; Krmíček et al., 2020), but significantly lower than those found for OIB-like and kimberlite magmas (e.g., Day et al., 2010; Digis, 2024; Maier et al., 2017; Tappe et al., 2020b). In this respect, our new data put the concentration range of previous studies to a new low level with the I-PGE values from 0.001 to 0.31 ppb and P-PGE values ranging 0.008–4.9 ppb. Therefore, the newly collected data (Fig. 4.5) corroborate the earlier observations which are based on a limited set of samples that very low HSE contents in carbonatites are a global feature which appears to be directly connected with the petrogenesis and the nature of carbonatite magmas.

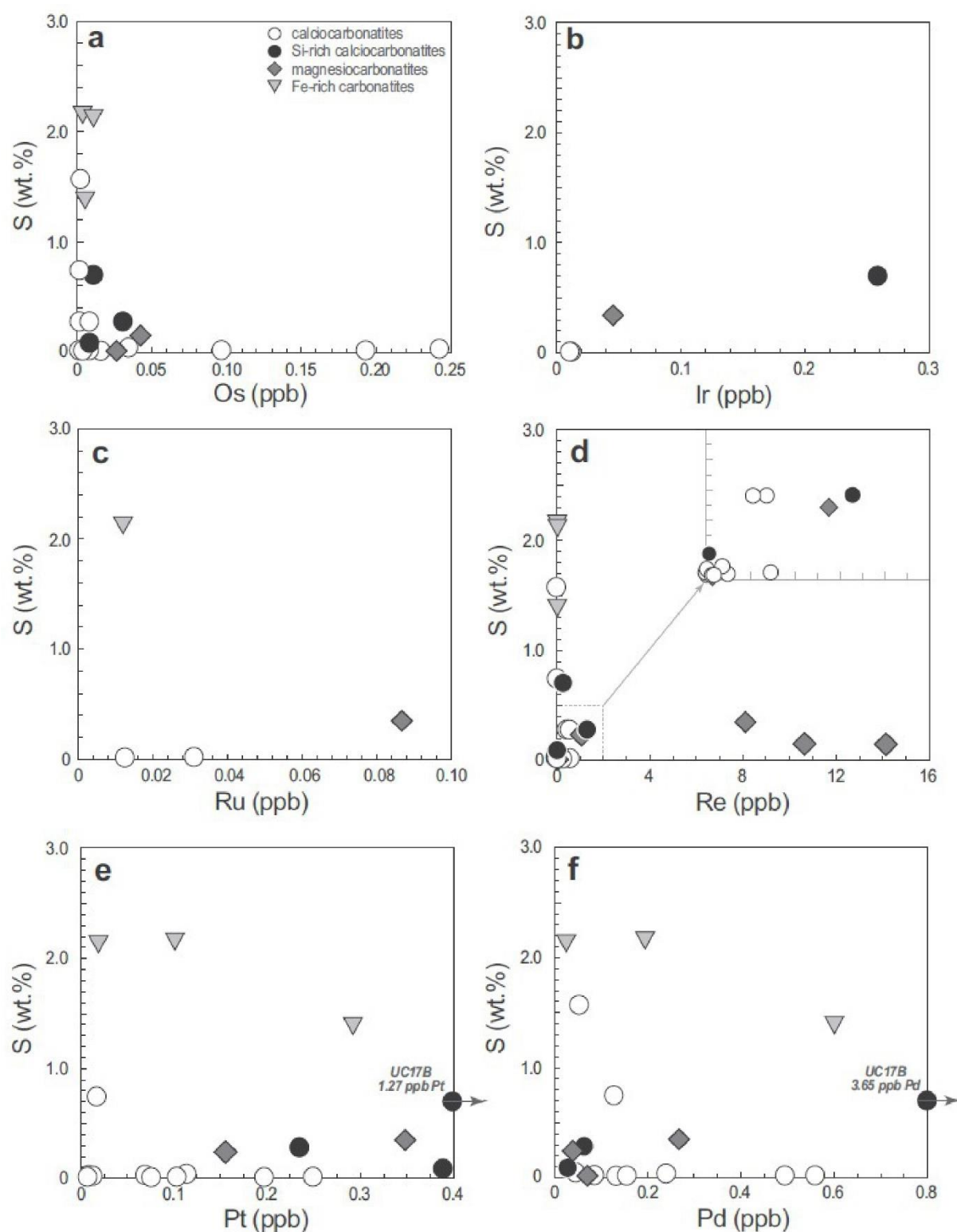


Fig. 4.5. Binary plots of Os, Ir, Ru, Pt, Pd, and Re versus S illustrating the absence of any direct relationship between individual HSE contents and sulfur suggesting that HSE contents are not directly driven by sulfur concentration.

Approximately 74% of carbonatite occurrences (Woolley and Kjarsgaard, 2008b) are linked with alkaline silicate rocks (e.g., nephelinites, kimberlites, lamproites, lamprophyres; Mitchell, 2005;

Tappe et al., 2006; Vladykin, 2009; Yaxley et al., 2022). With the exception of Newania magnesiocarbonatite that might represent a primary mantle-derived melt (Doroshkevich et al., 2010; Ray et al., 2013), all other carbonatites analyzed here occur in a close association with (ultra)mafic alkaline silicate rocks such as syenites, pyroxenites, nephelinites or ijolites (see section 2). This might indicate that the studied carbonatites may represent either cumulate rocks formed by fractional crystallization of carbonated alkaline SiO₂-undersaturated silicate melts (e.g., olivine nephelinite, melilite, kimberlite) or products of carbonate–silicate liquid immiscibility (Giebel et al., 2019; Ackerman et al., 2021; Yaxley et al., 2021). The former process is well-documented by the overwhelming presence of cumulate silicate rocks such as pyroxenites and/or dunites at the sampled localities while the latter is well-documented by carbonate and silicate melt inclusions (e.g., Solovova and Gernis, 2012; Guzmics et al., 2015). Thus, the low HSE contents in the analyzed carbonatites result from a complex interplay between primary melt source (e.g., peridotite, mixed peridotite–pyroxenite) and parental carbonated silicate or solely carbonatite melt.

Because sulfides are the principal PGE carriers in the upper mantle (Mungall and Brenan, 2014), the behavior of sulfur and sulfides during partial melting connected with the formation of S-saturated/undersaturated melts is of prime importance for a (re-)distribution of HSE between the primitive mantle and its melting products. Basaltic melts such as MORB formed by predominantly partial melting of peridotitic mantle (~10–15%; Elthon and Scarfe, 1984; Langmuir et al., 1992) are HSE-poor because they are S-saturated in the source (Mavrogenes and O'Neill, 1999), thus leaving PGE behind in residual sulfide phases. In comparison, alkaline and carbonated silicate magmas originate from a lower-degree (< 5 %) partial melting of the metasomatized mantle are likely sulfide undersaturated in the source. However, it has been postulated that sulfur contents of these alkaline silicate and carbonated silicate magmas at the sulfur saturation state are exponentially increasing with progressive oxidation state to as high as 1.4 wt. % sulfur at +2.3 Δ FMQ (Jugo, 2009) with prevalent sulfate in the source (Mavrogenes and O'Neill, 1999). Thus, this indicates the importance of oxygen fugacity for the extent of sulfur saturation and PGE extraction from the source.

Experimentally derived $D^{\text{sulfide/carbonate melt}}$ (Chowdhury et al., 2021) values for HSE exhibit a decreasing order from 10^5 for Os to 10^3 for Pt, and overall, they are consistently lower than those for sulfide/silicate equilibrium suggesting the enhanced capability of carbonated and carbonatite melts over silicate melts to sequester PGE from a sulfide-bearing source. This would also be in agreement with the reported HSE mobility during mantle metasomatism by volatile- and sulfide-rich melts (Alard et al., 2011; Aulbach et al., 2016) which was also suggested to be redox-controlled (Burness et al., 2020).

Alkaline silicate as well as carbonatite magmas are generally assumed to be volatile-rich and highly oxidized (up to +5 Δ FMQ; Tappe et al., 2006; Braunger et al., 2020) while the latter may

contain large amount of sulfur because experiments documented sulfur solubility in carbonatite melts about an order of magnitude higher than that reported for silicate melts (Jorgenson, 2017). High oxygen fugacity in the source should result in the transformation of sulfide to sulfate and it has been recently documented (He et al., 2020; Cai et al., 2021) that such a process can be associated with large-scale mobilization of PGE and their preferential removal into the co-existing carbonatite melt. Therefore, carbonatites and carbonated silicate melts might be capable to host significant amounts of PGE. However, the analyzed carbonatites and silica-rich carbonatites generally yield very low PGE contents (Tab 4.1). This also indicates that the observed low PGE in carbonatites should not be connected with the melt source itself, but rather with a melt evolution during its ascent.

Ascending carbonated and oxidized alkaline silicate melt will attain higher sulfur solubility at decreasing pressure (Mavrogenes and O'Neill, 1999). Considering significant fractionation of the parental melt at crustal conditions during progressive crystallization of silicate minerals (e.g., olivine, clinopyroxene) and/or interaction with ambient crustal rocks (Ackerman et al., 2021; Yaxley et al., 2022), the resulting carbonated silicate melt will therefore become increasingly enriched in S, CO₂ and CaO, but depleted in SiO₂. Under these circumstances, studies on melt inclusions indicate that the subsequent melt evolution may result in liquid immiscibility and separation of S-rich silicate melt and carbonatite melt or even separation of pure Cu–Fe sulfide melt (e.g., Guzmics et al., 2012) while we note that sulfur partitioning between silicate and carbonate melts can be complex (Guzmics et al., 2015). Nevertheless, considering high $D^{\text{sulfide/carbonate}}$ and $D^{\text{sulfide/silicate}} (> 10^3)$, the sequestered sulfide or S-rich silicate melt will be capable to sequester PGE leaving the co-existing Ca-rich carbonatite melt impoverished in PGE and S. This effect can be further facilitated by the formation of sulfur-bound PGE metallic clusters (Tredoux et al., 1995) in the separated S-rich silicate melt.

The anomalously high ΣPGE of ~5.2 ppb measured in Fe-rich silicocarbonatite UC17B (Iron Hill) representing the transition member between carbonated silicate and carbonatite melts indicates that variable physicochemical conditions (e.g., parental melt composition, temperature; e.g., Guzmics et al., 2015) during the the silicate–carbonate melt liquid immiscibility might be the key process controlling the S and PGE distribution of the resulting carbonatite melt. In comparison, the overall low PGE contents observed among different carbonatite types (calcio-, magnesio-, Fe-rich carbonatites) without any systematic difference suggest that subsequent evolution of carbonatite melt (calcite → dolomite → ankerite; Yaxley et al., 2022) does not play the determining role in PGE distribution. Yet, we cannot rule out that higher Pd and Pt contents found in two Cu–S-rich Phalaborwa Fe-rich carbonatites (TCBws3, TCBws5; Tab 4.1) might be connected with carbonatite melt evolution.

To conclude, very low PGE contents in carbonatite magmas can be best explained by the evolution of parental carbonated silicated melts. On the other hand, the possible reasons responsible

for different modes of I-PGE fractionation observed for calciocarbonatites ($\text{Os}_\text{N}/\text{Ir}_\text{N} > 1$) versus other carbonatite types with $\text{Os}_\text{N}/\text{Ir}_\text{N} < 1$ will be discussed in detail below.

4.5.3. Significance of I-PGE fractionation: source feature or evolution of parental alkaline silicate melt?

In spite of the fact that many carbonatites exhibit I-PGE contents below detection limits, calciocarbonatites and silicified calciocarbonatites uniformly show $\text{Os}_\text{N}/\text{Ir}_\text{N} > 1$ (**Type A**), while magnesiocarbonatites and Fe-rich carbonatites exclusively show $\text{Os}_\text{N}/\text{Ir}_\text{N} < 1$ (**Type B**). At the same time, almost all Ru values are below the detection limit (estimated to 7 ppt) suggesting that in the case of **Type A** carbonatites the normalized HSE patterns will show a negative slope from Os through Ir to Ru (Fig. 4.4). The depleted I-PGE patterns of the **Type B** carbonatites are similar to those of other mantle-derived magmatic rocks and can be ascribed to the observed I-PGE fractionation of **Type A** carbonatites with $\text{Os}_\text{N}/\text{Ir}_\text{N} > 1$ and, in particular, the pronounced Ru depletion. These features can be related to (i) the nature of the source, or (ii) PGE fractionation related to either parental carbonated silicate melt fractionation or evolution of calcite $\rightarrow$ dolomite $\rightarrow$ ankerite carbonatite melt. Ackerman et al (2019) argued that this phenomenon can reflect a source feature and explained this by preferential partitioning of I-PGE over P-PGE into carbonatite melts during the formation of S-saturated carbonatite melt at mantle conditions due to lower $D^{\text{Mss/Carb}}$ for I-PGE compared to P-PGE (Jorgenson, 2017). However, this explanation should be reconsidered in view of recent experimental data (Chowdhury et al., 2021) showing that $D^{\text{sulfide/carbonate}}$ for Os is higher than that for Ru. Consequently, modeled CO_2 -rich kimberlite and carbonatite magmas are characterized by $\text{Os}_\text{N}/\text{Ru}_\text{N} < 1$ unless the source contains unrealistically low (~ 5 ppm) sulfur content. While a similar mode of Os/Ir and Os/Ru elemental fractionation (Fig. 4.4) was described from several localities such as Deccan and Réunion basalts (Peters et al., 2017, 2016), flood basalts (Qi and Zhou, 2008) and lamprophyres (Gan and Huang, 2017) from China, the overall lack of $\text{Os}_\text{N}/\text{Ir}_\text{N}$ below unity in carbonated alkaline rocks suggests that this phenomenon most likely does not represent a source feature but is rather connected with parental melt fractionation. Nonetheless, we cannot rule out that I-PGE enrichment can also be partly related to the preferential dissolution of I-PGE carriers during melt/rock reactions between carbonated alkaline melts and ambient mantle lithologies. We note, however, that this process is generally pertaining to S-undersaturated melts (e.g., Ackerman et al., 2009; Lorand et al., 2004).

Although no plausible explanation was offered for the observed I-PGE fractionation in Deccan/Réunion basalts (Qi and Zhou 2008), large Ru depletion was ascribed to segregation of laurite (RuS_2) and/or Os–Ir–Ru alloy, along with olivine and spinel from the parental magma. Gan and Huang (2017) also stressed a complementary introduction of volatile Os by subduction-related melts/fluids. This process has been established to be plausible for a wide range of mafic

magmas showing variable negative Ru anomalies while the depleted residues (e.g., Cr-rich peridotites) commonly exhibit positive Ru anomalies and contain laurite and Os–Ir–Ru alloy enclosed in Cr-spinel (e.g., Kamenetsky et al., 2015). While this process would represent a feasible explanation for the extremely low Ru contents observed in almost all carbonatites (considering that they represent a liquid immiscibility product from highly fractionated silicate melts characterized by dominant olivine fractionation), it falls short to account for the observed Os–Ir fractionation ($Os_N/Ir_N > 1$) in calciocarbonatites and sometimes high Os contents (up to 0.24 ppb reported for Sevattur carbonatites; Ackerman et al., 2019).

As noted above and also corroborated by other studies (e.g., Chandra et al., 2019; Giebel et al., 2019; Ackerman et al., 2021), the studied carbonatites (except Newania) most likely originated through liquid immiscibility from carbonated silicate melts and calciocarbonatites in particular should represent the first type of carbonatites formed from Ca-rich liquids (Yaxley et al., 2022). Under these circumstances, the observed Os–Ir elemental fractionation can directly be related to lower $D^{sulfide/Carb}$ for Os (10^5) relative to Ir (10^6) as given by Jorgenson (2017) resulting in the preferential removal of Ir over Os during the segregation of calcite-normative melts from the co-existing S-rich silicate melts or even Cu–Ni-rich melts. This effect, together with the paralleled Os enrichment in Sevattur samples, can be further facilitated by the highly oxidized and fluid-rich nature of carbonatite melts because Os is highly mobile in oxidized fluids (Brandon et al., 1996) and it is strongly partitioned into the fluid/volatile phase at moderate temperatures (Yudovskaya et al., 2008).

4.5.4. Constraining the nature of parental melt sources from Re–Os systematics of carbonatites

It appears from the discussion in Section 5.1 that the Re–Os systematics of carbonatites can be severely modified by late-stage hydrothermal processes leading to either removal of both Re and Os or the addition of Re. Consequently, these effects result in commonly negative γ_{Os} values observed in this study indicating large-scale perturbation of the Re–Os systematics irrespective of the age or geotectonic settings of the investigated samples (Tab 4.1). This is in contrast to the limited data reported for oceanic carbonatites (Escrig et al., 2005; Widom et al., 1999) and also to what was observed in the continental Tamil Nadu carbonatites where (Ackerman et al., 2019) documented that Re–Os elemental and isotope systematics reflects parental melt fractionation and a heterogeneous source mantle characterized by the presence of a recycled crustal component. On the other hand, this observation agrees with studies of Pearson et al. (1995) and Tappe et al. (2020b) on carbonatites from cratonic settings, and in this respect, our new enlarged dataset collectively highlights a limited potential of global Re–Os systematics of carbonatites for the evaluation of parental mantle sources. This is unfortunate since several studies closely linked radiogenic $^{187}Os/^{188}Os$ signatures obtained for

different types of alkaline silicate rocks such as lamprophyres, nephelinites, and basanites with carbonatite metasomatism, plausibly related to oxidation of a mantle wedge by recycled carbonates (e.g., Cai et al., 2021; Gan and Huang, 2017). The radiogenic $^{187}\text{Os}/^{188}\text{Os}$ nature of carbonatite melts (>0.17) has been also inferred by Ackerman et al. (2019) and Escrig et al. (2005), corroborating previous findings of carbonated peridotite xenoliths with radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values (>0.13 ; Alard et al., 2011, He et al., 2020). Establishing the primary Os isotope compositions of carbonatites is of prime importance because carbonatite metasomatism possibly plays a determining role in establishing $^{187}\text{Os}/^{188}\text{Os}$ composition of the Earth's mantle as a consequence of extreme mobility of carbonatite liquids (e.g., Kono et al., 2014; Ritter et al., 2020; Rudnick et al., 1993; Wallace and Green, 1988). Considering that differentiation of parental silicate melts and late-stage effects have an apparent impact on the Re–Os contents but less likely on their primary $^{187}\text{Os}/^{188}\text{Os}$ signatures, we may consider Os isotope data for the youngest carbonatite samples (<70 Ma) that show no obvious signs of Re–Os perturbation (e.g., presence of late-stage sulfides, etc.) as potentially reliable. In this respect, we further emphasize that even the possible modification of Re and Os budgets in these samples cannot lead to pervasive modification of initial $^{187}\text{Os}/^{188}\text{Os}$ values since their rather young emplacement ages prevent sufficient formation of ^{187}Os because of the long decay time of ^{187}Re . When the sample AC03D from Tororo is omitted due to the presence of secondary pyrite (see Section 4.1), in agreement with its negative $\gamma_{\text{Os(i)}}$ value (Tab 4.1), five carbonatites from Amba Dongar and carbonatite sample AC01G from Sukulu exhibit variable but radiogenic initial $^{187}\text{Os}/^{188}\text{Os}$ values (~ 0.76 to 5.6) with corresponding $\gamma_{\text{Os(i)}}$ values ranging from ca. $+400$ to $+4,000$ (Fig. 4.6); we note large errors associated with the calculations comprising all uncertainties (see Section 3) or a nugget effect. At both localities, carbonatites represent products of liquid immiscibility from the parental carbonated silicate melts (Chandra et al., 2019; Ackerman et al., 2021) with 2–8 % assimilation of local Archean basement gneiss reported for Amba Dongar (Chandra et al., 2019). The lower crustal lithologies can yield variable $^{187}\text{Os}/^{188}\text{Os}$ compositions (e.g., Barth et al., 2002; Peucker-Ehrenbrink and Blum, 1998; Saal et al., 1998) with extreme present-day γ_{Os} values of up to $\sim +19,000$ reported for crustal sulfides (Aulbach et al., 2010). Nevertheless, the data collected so far indicate a variation of $^{187}\text{Os}/^{188}\text{Os}$ ratios in the continental crust in the range between ~ 0.5 and ~ 1.9 and $[\text{Os}] \leq 50$ ppt (Peucker-Ehrenbrink and Jahn, 2001 and references therein). Thus, the reported degree of crustal assimilation for Amba Dongar parental melts cannot account for the observed highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ signatures of carbonatites. This is also in agreement with the initial $^{187}\text{Os}/^{188}\text{Os}$ value of ~ 0.73 found for Sukulu carbonatite AC01G in spite of its mantle-like Sr–Nd isotope signature (Ackerman et al., 2021) and radiogenic $^{187}\text{Os}/^{188}\text{Os}$ signature (2.1) of Kovdor carbonatites where no crustal contamination has been assumed (Schweitzer, 2019).

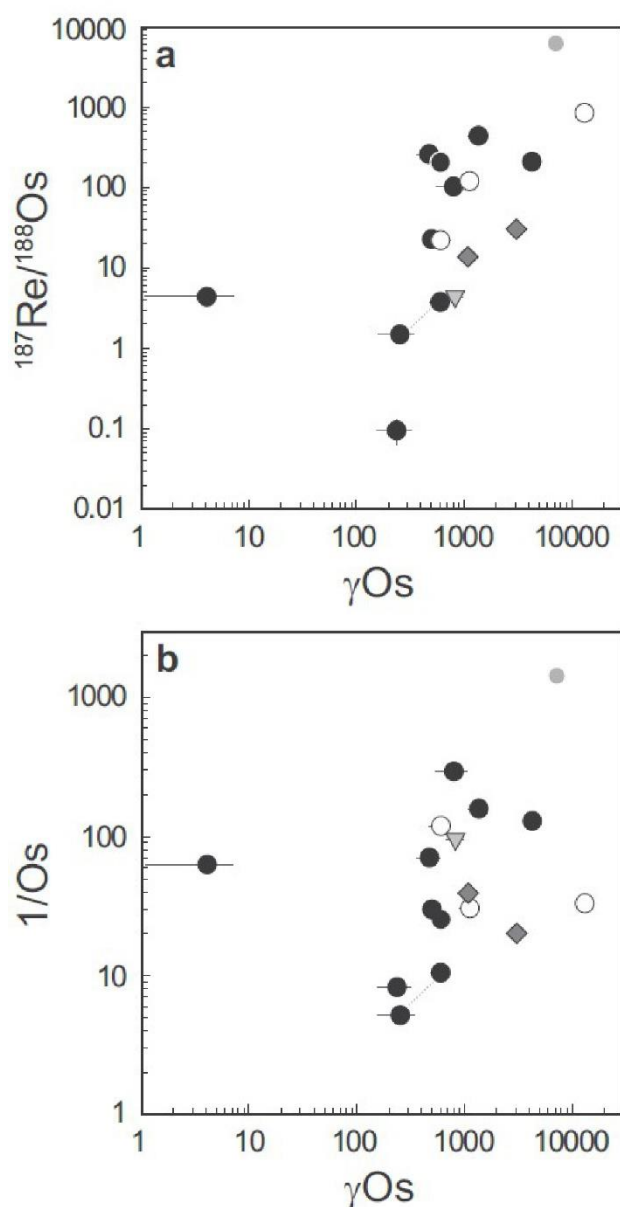


Fig.4.6. The γOs versus $^{187}\text{Re}/^{188}\text{Os}$ (a) and $1/\text{Os}$ (b) relationships. Note, that the uncertainties represented by 2σ values (Table 4.1) are usually smaller than symbol sizes.

Collectively, the limited Re–Os data obtained so far that can most likely be ascribed to primary source signatures uniformly indicate the radiogenic $^{187}\text{Os}/^{188}\text{Os}$ nature of carbonatite melts. Whether this phenomenon is connected with the presence of recycled oceanic crust (e.g., eclogites) with variable but radiogenic $^{187}\text{Os}/^{188}\text{Os}$ signatures at the source or with carbonatite metasomatism itself remains uncertain. The results indicate that the Re–Os system was not closed for the entire time during the ascent and that it was contaminated *en route* to the surface and/or suffered from post-magmatic alteration.

4.6. Conclusions

- (1) We provide a comprehensive dataset of combined HSE abundances and Re–Os isotope compositions from 11 carbonatite occurrences with the emplacement ages ranging from ~2060 to <40 Ma attesting to global variation of HSE systematics in carbonatite melts.
- (2) The majority of carbonatites contain very low ΣPGE <1 ppb, in agreement with very low sulfur contents, suggesting a limited presence of heterogeneously distributed HSE-bearing carriers in carbonatites. Conversely, high Re contents revealed for several samples are intimately linked with the presence of molybdenite.
- (3) Globally very low PGE contents in carbonatites can be best explained by the evolution of parental carbonated silicate melts and PGE exhaustion into sulfide and/or S-rich silicate melts during carbonate–silicate liquid immiscibility

(4) Calciocarbonatites and silicified calciocarbonatites uniformly show $\text{Os}_\text{N}/\text{Ir}_\text{N} > 1$ as a consequence of the separation of calciocarbonatite from CO_2 -rich liquids and preferential removal of Os over Ir during the separation of calcite-normative melts from coexisting S-rich silicate melts.

(5) The Re–Os isotope systematic have been severely affected by late-stage hydrothermal processes and >35% of the samples had to be excluded due to unrealistic γ_Os values (ranging from $-110,000$ to $+14,000$). The wide range of $^{187}\text{Os}/^{188}\text{Os}$ ratios of carbonatites appears to reflect either the presence of recycled crust in the mantle source or previous carbonatite metasomatism of the source mantle.

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Chapter 5

5.1. Summary and implications

Although carbonatites have been recognized for about one and a half century, their significance extends far beyond scientific interest since they play a crucial role in economic geology as a main REE carrier, making them essential for understanding the Earth's science potential. In particular, carbonatites provide a unique window to Earth's processes such as the cycling of carbon, mantle metasomatism and generation of CO₂-rich melts.

Three main carbonatite groups were determined (Chapter 2) based on their Sr and Nd isotopic signatures that can be related to the nature of their source. The majority of carbonatites (about 40 %) belong to the so-called **Group 1**. This group belongs to the first quadrant of the Sr-Nd space which is universally occupied by mantle-derived melts without any or with perhaps minor modification during their ascent to lower crust or to the Earth's surface. In contrast, carbonatites from the **Group 2** have apparently incorporated recycled sedimentary or marine material delivered into their mantle source via subduction. The presence of sediments or carbonates in their sources was unequivocally evidenced by their distinctive C–O isotope compositions as well as some non-traditional stable isotope (e.g., Mg, B) signatures. Those carbonatites provide evidence of active subduction for at least the last 2 billion years. The estimated timeframe for the onset of subduction processes and plate tectonics can be further refined with collective evidence from the **Group 3** carbonatites. Those carbonatites inherited low Rb/Sr and Sm/Nd, in particular, the latter reflected in highly unradiogenic time-integrated ϵ_{Nd} character that cannot be explained by solely melting of an enriched mantle source. At present, the **Group 3** consists of samples from eight different carbonatite occurrences with different ages of formation spanning from 76 Ma to 2 Ga. Calculated medians of these carbonatite bodies plotted in $^{143}\text{Nd}/^{144}\text{Nd}$ vs. age s display a tight regression line with $r^2 = 0.94$ and intersecting the CHUR line at ~2.8 billion years ago. Due to such a large coefficient of covariation in samples coming from different geographic areas, with different emplacement ages, and formed in different geological settings, I suggest that their sources had to undergo a broadly similar evolution process. One of the plausible explanations is the subduction or delamination of the Archean oceanic crust into the mantle associated with melting and resulting in newly formed slab-derived melts (with a composition similar to TTG/sanutikoids) further interacting with the mantle lithologies. Consequently, this metasomatized mantle source parental to the **Group 3** has remained isolated since. The model (Fig. 2.7) quantifies that the admixture of 2-6 % slab-derived TTG with a depleted mantle source can results in the observed unradiogenic Nd isotopic signatures of the **Group 3** carbonatites.

The pioneering study combining Re–Os isotopic compositions along with highly siderophile element (HSE) systematics was performed on carbonatites and associated alkaline rocks from Tamil Nadu in South India. One of the main goals was to prove the veracity of the analytical protocol used to

determine the concentrations of HSE and assess the possible volatile loss of Os. In this respect, the robustness of the protocol used was confirmed by utilizing different mineral acids during decarbonatization at different temperatures prior to sample decompositions (Tab 3.1). The study of Tamil Nadu carbonatite–silicate complexes confirmed generally low contents of HSE at sub-ppb levels in carbonatites, which was attributed to the retention of sulfide phases in the source after separation of carbonatite melts by liquid immiscibility. The newly determined $^{187}\text{Os}/^{188}\text{Os}(\text{i})$ and $^{187}\text{Re}/^{188}\text{Os}$ ratios ranging from unradiogenic/slightly radiogenic values (0.186 and 0.4, respectively) to highly radiogenic (10 and 217, respectively) indicate that calciocarbonatites from Tamil Nadu (Chapter 3) have been derived from a carbonated peridotite source with the addition of less than 10% of recycled components. The higher content of HSE found in silicocarbonatites was attributed to a yet unrecognized platinum-bearing mineral phase. The silicocarbonatites likely originated from the interaction of enriched mantle-derived melts with previously fenitized pyroxenites. Local silicate alkaline rocks were considered as a derivative from an entirely different source than carbonatites. Among the notable results from Ackerman et al. (2017) was the possible capability of some carbonatites to concentrate IPGE over PPGE as $\text{Os}_\text{N}/\text{Ir}_\text{N}/\text{Ru}_\text{N} > 1$, which is the opposite of what is normally observed in other mantle-derived melts. In an extended set of samples, supra-chondritic $\text{Os}_\text{N}/\text{Ir}_\text{N}$ ratios (1.4–15) were found not only in calciocarbonatites, but also in silicified calciocarbonatites while magnesiocarbonatites and ferro/ferruginous carbonatites have sub-chondritic $\text{Os}_\text{N}/\text{Ir}_\text{N}$ signatures. We argue that this elemental fractionation is a result of the separation of calciocarbonatite melts from CO_2 -rich liquids during which Os will be preferentially removed from the melt compared to Ir. The reason why this phenomenon can only be observed in silicified calciocarbonatites and calciocarbonatites is that calciocarbonatites represent the first carbonatite fraction formed from Ca-rich liquids. The $^{187}\text{Os}/^{188}\text{Os}(\text{i})$ and $^{187}\text{Re}/^{188}\text{Os}$ ratios of carbonatites worldwide display an even more radiogenic character reaching up to 17 and 26,000, respectively. Such values are too extreme to be explained by the possible presence of recycled components such as in Tamil Nadu. In Polák et al. (in press), these highly radiogenic values were attributed to the disturbance of the Re–Os system by hydrothermal alteration resulting in either the removal Re and Os or the addition of Re underscoring that Re–Os systematics of carbonatites is sensitive to late-stage modifications. Low HSE contents found in carbonatites worldwide confirm the previous findings that liquid immiscibility of a carbonatite melt from parental S-rich silicate melts or carbonatite/silicate melt separation with sulfides sequestered into silicate melt plays the dominant role in the evolutionary pathways of HSE systematics in carbonatites. Given these above observations, it can be concluded that carbonatites are generally not capable of significantly modifying the total budget of HSE in the Earth's mantle via carbonatite metasomatism. The mineral phase in carbonatites where HSE are abundant was not discovered. However, data from Ackerman et al. (2019) and Capobianco et al. (1994) confirmed that HSE are not concentrated in magnetite. The scale of the nugget effect indicates that HSE are

rather heterogeneously dispersed as micro/nanophases in the form of sulfides, tellurides, or metal alloys.

Even though carbonatitic melts are not capable of significantly modifying the total budget of HSE in the Earth's mantle, the HSE data for global carbonatites indicate that carbonatite-like metasomatism might, at least in part, be responsible for non-chondritic HSE elemental ratios (e.g., intra-IPGE fractionation), sometimes observed in mantle xenoliths. The obtained $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ data for global carbonatites (Chapter 4), while still limited, cannot be unequivocally explained by the specific nature of the melt source, variable incorporation of recycled oceanic crust (e.g., eclogite) and/or previous carbonatite metasomatism. On the other hand, several features such as the lack of correlation between $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$, the presence of common negative γ_{Os} values, a wide range of Re contents that are sometimes related to the late-stage addition of molybdenite and/or pyrite, indicate non-closed behavior and perturbation of the Re–Os systematics ultimately leading to significant changes. Therefore, it appears that Re–Os isotopic data for carbonatites have only limited potential to unravel the petrogenesis of carbonatitic melts and their significance for the Re–Os evolution of the Earth's mantle.

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