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Carbonatites complexes and associated REE mineral system: Significance in modern technology

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ABSTRACT

Carbonatites, comprising both intrusive igneous and hypabyssal rocks, are among the major reserves of rare earth elements (REE) on Earth, and are hence critical for modern technology. Major REE minerals in these rocks include bastnaesite, monazite, xenotime, pyrochlore and apatite. REE important military applications, computer displays, sonar, hybrid vehicles, digital cameras, etc. REE mineralization is usually associated with potassic rocks, carbonatite and nephelinitic rocks. In Western Australia, important carbonatite systems include Copperhead, Mt Weld and the Gifford Creek ferrocarbonatite complex. In terms of whole-rock alteration, fenitisation, which occurs in aureoles of carbonatite and alkaline complexes. Associated mineralisation is usually related to alkali metasomatism in anorogenic ring complexes, in which unusual concentrations, apart from REE, contain F, Zr, Ba, Nb, Th, U, Ta and W. Ring complexes of the ijolite-carbonatite and zircon. Pyrochlore generally occurs in sodic metasomatized peralkaline granites. Good examples of REE mineral systems are the Pilanesberg Complex, the Pienaars River Complex and the Lolekop carbonatite complex.

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Research Highlights

- REE minerals in carbonatite becoming increasingly important in diverse applications.
- Important carbonatite systems occur in Western Australia.
- Anorogenic ring complexes also carry anomalous F, Zr, Ba, Nb, Th, U, Ta and W.

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1 Introduction

Carbonatites are becoming increasingly important for a number of reasons, such as their content of rare earth elements (REE) minerals and their industrial use as catalysts, magnets, batteries, metallurgy etc. (Goodenough, 2017; Pirajno and Yu, 2022 and references therein). REE are also known as the lanthanides, are comprised of metallic elements with atomic numbers ranging between 57 and 71 (Table 1): La, Ce, Pr, Nd, Sm (the 'light' REEs) and Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, where Ho to Lu are often referred to as the 'heavy' REE. Yttrium is also included in REE because it shows similar chemical properties and generally occur in the same ore deposits. The most common minerals that are rich in REE are bastnäsite ((Ce/Nd/Y/REE) (CO₃) F), monazite ((Ce, La, Nd, Th) PO₄), xenotime (YPO₄) and allanite ((Ce,Ca,Y,La)₂(Al,Fe+3)₃(SiO₄)₃(OH)). The REE, based on their atomic number are divided into Light REE and Heavy REE, with Yttrium included in the latter because it shares chemical similarities.

Carbonatites are a distinctive rock type that originate from metasomatised Sub-continental Lithospheric Mantle (SCLM) in specific tectonic settings, usually rift systems, and occur as plugs, sills, dykes, sub-volcanic intrusion in ring complexes, cone sheets around alkaline volcanoplutonic complexes. Carbonatites are also becoming increasingly important due to their potential to hold economic quantities of Th, U and REE. The rock-forming minerals of carbonatites typically include calcite, dolomite, ankerite and siderite associated with variable amounts of bastnaesite, apatite, magnetite, monazite, xenotime, barite, pyrochlore as well as a range Nb-, Th- and REE-bearing minerals.

Major REE minerals comprise the following: bastnaesite which is considered the most important REE ore, monazite (REE(PO₄) (50-78%), xenotime (YPO₄) (up to 65%), apatite (Ca₅(PO₄)₃(F, CI, OH). REE are very important for modern technology because they contribute to of high energy efficiency, such as compact fluorescent light, and hybrid vehicles and flat panel displays and digital cameras. In addition, REE metals have also important military applications (e.g. anti-missile defence, radar, computer displays, sonar, missile guidance, jet fighter engines, rechargeable batteries, etc.). REE mineral systems can be of magmatic origin (carbonatite, peralkaline, pegmatite) or sedimentary associated (e.g. placers, phosphorites ion adsorption clays) (Qiu et al., 2019; Wu et al., 2021). Fig. 1 displays the REE minerals and hosting lithologies (after Chakhmouradian and Wall, 2012).

REE mineralization is generally associated with potassic rocks, carbonatites and nephelinitic rocks. Highly fractionated, meta-aluminous and peralkaline granite intrusions can be enriched in rare earth elements, which is

augmented by chlorine and fluorine-rich hydrothermal fluid activity. Surficial clays and laterites may also have high concentrations of rare earth elements (Lal, 2017). The known distribution of REE occurrences and deposits (including current mines) is shown in Fig. 2 from the British Geological Survey.

The main host of REE mineralisation is carbonatite. Carbonatites comprise intrusive igneous and hypabyssal rocks, igneous rocks in which carbonate minerals are primary. Apatite and pyrochlore are generally considered essential; accessory minerals include siderite, calcite, dolomite and ankerite, whilst less common accessory minerals include Mg-rich magnetite, phlogopite and pyrite. An idealised carbonatitic volcano-plutonic system is shown in Fig. 3.

2 Three carbonatites in Western Australia: diversity in one rock type

2.1 Copperhead

The Copperhead carbonatite is part of a small (110 m \times 80 m) syenite plug in the Alice Downs area, 70 km north of the town of Halls Creek in the East Kimberley (Fig. 4) (Rugless and Pirajno, 1996).

This syenite-carbonatite ring-like system, discovered and reported by Rugless and Piraino (1996), is located in the Paleoproterozoic Lamboo Complex of the Halls Creek orogeny (Tyler et al., 2012). The Lamboo complex has three northeast-trending tectono-stratigraphic terranes. A western terrane comprises volcanics, layered mafic intrusions and granitoids with zircon ages of ca 1.85-1.86 Ga. The central terrane comprises granitoids and gabbros dated at 1.82 Ga which intrude metavolcanics and metasedimentary rocks of the Tickalara Metamorphics. The eastern terrane includes metavolcanic and metasedimentary rocks of the Halls Creek Group. The Lamboo Complex is dominated by the transcurrent Halls Creek Fault that has been active from the Palaeoproterozoic until perhaps, Devonian times. Griffin (1990) recognised a number of periods of deformation in the Lamboo Complex and field evidence indicates that the Copperhead syenitecarbonatite was emplaced after D3 and possibly pre- or syn-D4. The ages of D3 and D4 are thought to be Neoproterozoic (Griffin, 1990). The emplacement of Copperhead appears to be related to a series of northwesterly trending dilatant Riedal faults exhibiting sinistral movement related to and occurring 13 km northwest of the Halls Creek. The metamorphic host rocks of the Copperhead intrusion are cut by a series of E-W-trending, and subsequently NNWtrending, faults, with the latter clearly sinistrally offsetting the intrusive Panton Sill, to the south (Rugless and Pirajno, 1996). The NNW trending faults area consistent with dilatant "R" Reidel shears related to the Halls Creek /Springvale transcurrent shear couplet. This late D3 to D4 dilation

Ζ		Name	Etymology		
57	La	Lanthanum	from the Greek "lanthanon," meaning I am hidden.		
58	Ce	Cerium	for the Roman deity of fertility Ceres.		
59	Pr	Praseodymium	from the Greek "praso," meaning leek-green, and "didymos," meaning twin.		
60	Nd	Neodymium	from the Greek "neo," meaning new-one, and "didymos," meaning twin.		
61	Pm	Promethium	for the Titan Prometheus, who brought fire to mortals.		
62	Sm	Samarium	for Vasili Samarsky-Bykhovets, who discovered the rare earth ore samarskite.		
63	Eu	Europium	for the continent of Europe.		
64	Gd	Gadolinium	for Johan Gadolin (1760–1852), to honor his investigation of rare earths.		
65	Tb	Terbium	for the village of Ytterby, Sweden, where the first rare earth ore was discovered.		
66	Dy	Dysprosium	from the Greek "dysprositos," meaning hard to get.		
67	Ho	Holmium	for Stockholm (in Latin, "Holmia"), native city of one of its discoverers.		
68	Er	Erbium	for the village of Ytterby, Sweden.		
69	Tm	Thulium	for the mythological land of Thule.		
70	Yb	Ytterbium	for the village of Ytterby, Sweden.		
71	Lu	Lutetium	for Lutetia, the city which later became Paris.		
Source: http://en.wikipedia.org/wiki/Rare_earth_element.					

Table 1. The Rare Earth Elements and their etymology.

event may have accompanied the intrusion of the syenitecarbonatite. U-Pb SHRIMP age of zircons from the Copperhead syenite-carbonatite, yielded 1821 ± 4 Ma (Jaques, 2008) which, within error, not too dissimilar from the age of the Hart Dolerite large igneous province (Piraino and Hoatson, 2012). Rugless and Pirajno (1996) recognised three zones: (1) an inner albitised syenite zone (hereafter referred to as albitite) consisting mainly of medium- to coarse-grained albite and probably representing a fenitised intrusive alkaline svenite stock; (2) an outer albite - carbonate fenitic zone consisting of fine- to medium-grained albite and carbonate and (3) carbonate breccias along the eastern margin of the intrusive. Leucocratic, albite-rich, dykes cut the Copperhead syenite-carbonatite intrusion. The guartzo-feldspathic country rocks have been albitised adjacent to the intrusive and have locally preserved a relict foliation.

2.1.1 Petrographic and cathodoluminescence analyses

The albitite of the *inner zone* is characterised by a hypidiomorphic granular texture, containing two generations of albite including a multiply twinned subhedral phase that has been overprinted by a relatively untwinned anhedral albite. This assemblage is moderately deformed with kinking of platy muscovite and the neo crystallisation/annealing of albite along microfractures. Textural relationships suggest that the albite was formed during two episodes of sodic metasomatism. Rutile needles paralleling rectilinear amphibole crystallographic planes have been overprinted by both albite and carbonate. Accessory phases include apatite, zircon, monazite and allanite. Accessories include

Ti-Fe oxides, Th-rich monazite and trace gold, possibly associated with a phyllosilicate phase. Apatite fluoresces blue under cathodoluminescence and confirms an alkaline origin (Mariano, 1989). The outer zone represents more intense metasomatism of a fine to medium grained host, and is dominated by anhedral, poorly twinned and checkerboard textured albite. Calcite (up to 22 vol%), occurs interstitially and is intimately associated with subhedral albite. Incipient sericite/muscovite alteration of plagioclase, accessory platy biotite and thuringite (Fe-Mg chlorite) are products of a retrograde hydrothermal alteration overprint. Apatite, thorite, monazite and zircon represent accessory phases. Cathodoluminescence examination shows that both relict igneous apatite (yellow fluorescence) and finely dispersed alkaline apatite (blue fluorescence). The carbonate breccia occurs as a number of pods (up to 20 m²) consisting of coarse-grained calcite. The carbonate breccia includes autobrecciated carbonate material as well as fragments of the host intrusive that have not been isolated and identified in detail to date. The eastern margin of the main carbonate pod is intensely altered to sericite/platy muscovite, probably a hydrothermal retrograde phase. Limonite/goethite aggregates (after original sulphides?) are dispersed through the sericitised carbonate. Apatite is an accessory and fluoresceses blue under cathodoluminescence. Rugless and Piraino (1996) interpreted this carbonate material as a calciocarbonatite. Fenitised country rock is dominated by albite occurring as a fine to medium grained (up to 0.6 mm) mosaic associated with interstitial platy muscovite retrogressed to fibrous chlorite/secondary biotite. Oriented leucoxenerutile aggregates are probably after biotite, and mimic a

Mineral nameª Formula	Relevant rare elements (range or max. value)	Major deposit type(s)º
Bastnäsite REECO₃(F,OH)	53-79 wt%ΣREO; ≤2.8 wt% ThO ₂	CRB; HMD
Parisite CaREE₂(CO₃)₃(F,OH)₂	58-63 wt%ΣREO; ≤4.0 wt% ThO ₂	CRB; HMD
Synchysite CaREE(CO ₃) ₂ (F,OH)	48-52 wt%ΣREO; ≤5.0 wt% ThO₂	CRB; HMD associated with CRB and granites
Ba–REE fluorocarbonates ^b Ba _x REE _y (CO ₃) _{x + y} F _y	22-40 wt%ΣREO; ≤0.7 wt% ThO₂	HMD; CRB
Monazite (REE,Th,Ca,Sr)(P,Si,S)O ₄ solid solution to cheralite (Ca,Th,REE)PO ₄	38-71 wt%ΣREO; ≤27 wt% ThO ₂ ; ≤0.8 wt% UO ₂	CRB; HMD; granitic pegmatites; Fe oxide-phosphate rocks; laterites; placers
Xenotime (REE,Zr)(P,Si)O ₄	43-65 wt%ΣREO; ≤8.4 wt% ThO ₂ ; ≤5.8 wt% UO ₂	Granites and pegmatites; HMD associated with granites; laterites; placers; rarely CRB
Churchite REEPO₄•2H₂O	43-56 wt%ΣREO; ≤0.3 wt% ThO ₂	Laterites
Fergusonite REENbO₄	43-52 wt%ΣREO; ≤8.0 wt% ThO ₂ ; ≤2.4 wt% UO ₂	Granites and pegmatites; HMD associated with peralkaline rocks
Loparite (Na,REE,Ca)(Ti,Nb)O₃	28-38 wt%ΣREO; ≤1.6 wt% ThO ₂	Peralkaline feldspathoidal rocks

Fig. 1. REE minerals and hosting lithologies. CRB carbonatite; HMD Hydrothermal metasomatic (after Chakhmouradian and Wall, 2012).

relict schistosity in the metasomatised country rocks. The carbonate content and incipient sericite alteration of the plagioclase matrix decrease markedly away from the intrusive. Accessories include magnetite, zircon, monazite, tourmaline, thorite, thorogummite enveloped by a Ti/Fe oxide, possible Zr-rich thorosteenrupine as well as unidentified secondary Fe/Ni and Fe/Cu minerals. Apatite is zoned, with a blue fluorescent (alkaline) core and yellow flourescent (igneous) rim under cathodoluminescence examination.

2.1.2 Albitisation-fenitisation

The albitite of the *inner zone* is typified by pervasive albitisation introduced in at least two generations, that has probably disguised the host intrusive, which Rugless and Pirajno (1996) interpreted to be a quartz syenite. Albitisation represents a subsolidus metasomatic process during which the development of Na-rich fluids results in textural and mineralogical changes of the host lithology (Pirajno, 2013). The albite-carbonate assemblage of the *outer zone* is somewhat enigmatic, although trace element/REE geochemistry and petrography reported in Rugless and Pirajno (1996) seems to confirm a continuum with the metasomatism of the albitite core. A progression from quartzalbite-orthoclase normative composition representing the intrusive core (*inner zone*) to an albite-nepheline normative composition representing the *outer zone* is consistent with fenitisation of silica oversaturated rocks. It was pointed out by Rugless and Pirajno (1996) that desilicification of



Fig. 2. World map showing distribution of Rare Earth Element deposits (kindly provided by British Geological Survey).

the *outer zone*, which now comprises an intimate association of albite and carbonate differs from documented sodic fenites that can also contain alkali feldspar, aegirine to aegirine augite, magnesio-arfvedsonite to eckermannite and biotite as exemplified by the Lueshe and Kirumba carbonatites in eastern Zaireand complexes in the Cape Verde and Canary Islands (Le Bas, 1981). This may be explained by a metaluminous/peraluminous rather than peralkaline parental magma (Kinnaird and Bowden, 1991).

Sodic metasomatism is considered evidence for deeper intrusions with the progression to alkali metasomatism at shallower erosional levels (Kinnaird and Bowden, 1991), as observed for the Gifford Creek ferrocarbonatite complex (Section 2.3). Additional evidence for the depth of a complex may be provided by the areal extent of fenitisation. Gittins (1989) suggested that fenitisation is unlikely to occur below a critical depth within the crust, as exemplified by carbonatites that have crystallised at a considerable depth in granulite terrain of Northern Ontario, all of which are associated with minor metasomatism. However for a relatively small intrusive plug, such as Copperhead, which is associated with an extensive zone of sodic fenitisation both within the intrusive and the adjacent country rocks, it is suggested that unroofing of the plug may have been relatively minor based on the development of nearcontemporaneous hydrothermal alteration of the intrusive.

2.1.3 Deformation and hydrothermal alteration

Hydrothermal alteration to sericite, chlorite and biotite that may have been focussed by structures that were active during the waning phases of the intrusive. Examination of the RAB chips from the CCR 1 & 2 drill holes (Rugless and Pirajno, 1996) shows incipient brittle/ductile fracturing of the outer zone albite-carbonate assemblage. Secondary carbonate has penetrated along. Localised fibrous sericite/platy muscovite and/or stellate chlorite aggregates have also replaced the albite-carbonate host assemblage. Fine polygonal secondary plagioclase aggregates and platy biotite, observed in the RAB chips, are also interpreted to have a metasomatic-hydrothermal origin. Replacement of the main carbonatite pod by



Fig. 3. An idealised nephelinitic-carbonatitic volcano-plutonic complex (after Le Bas, 1981). Apatite and pyrochlore are often considered essential. Accessory minerals are mainly: siderite, calcite, dolomite, or ankerite. Less common accessory minerals: Mg-rich magnetite, phlogopite, and pyrite.

sericite/muscovite within the Copperhead intrusion is associated with enhancement of LILE and trace elements such as Ba, Li, Ga, Zr, Nb, Sn and As (Rugless and Pirajno, 1996), confirming the role of a hydrothermal cell, perhaps involving convecting groundwater. Significantly this later alteration phase has not affected fenitised-albitised country rocks occurring immediately west of the intrusive (Fig. 4).

2.1.4 Mineralisation

Rugless and Pirajno (1996) reported that the Copperhead intrusion does not show economic enrichment of REE, P and Nb, although a general increase in incompatible and REE elements towards the margins of the intrusion and, in the fenitised country rock is observed. Rock chip sampling confirmed the presence of anomalous REE, with Zr (up to 290 ppm), Y (up to 76 ppm), Nb (up to 34 ppm), Ce (up to 600 ppm) and Ga (up to 62 ppm). Thorium, Ce, Fe/Ti, Fe/Cu and Fe/Ni bearing minerals have been identified in SEM studies. Results from the followup RAB drilling programme (drill holes CCR 1 & 2, also reported in Rugless and Pirajno (1996) showed slightly anomalous REE values (i.e. Ce 148 ppm, La 86 ppm), within the *outer zone*). Copper and Zn anomalous gossans occur peripheral to the Carbonatites and associated REE mineralisation. General enhancement of the incompatible and LREE elements within the carbonatites and associated REE mineralisation is qualitatively comparable with the Cummins Range carbonatite and the Brockman Formation trachytic ash flow tuff, both in the Halls Creek



Fig. 4. Geology and geochemistry of the Copperhead Albitite Carbonatite Complex, east Kimberlite, Western Australia (after Rugless and Pirajno, 1996).

orogen (Downes et al., 2014). Chondrite normalised spider plots of the Copperhead carbonatite exhibit patterns of LREE enrichment and HREE depletion, which may reflect HREE and LREE preferential distribution into mineral species during crystallisation. The *inner zone* hydrothermally altered *outer zone* and the carbonatite show positive Eu anomalies that can be attributed to modifications related to post-magmatic processes, which in this case are dominated by Na metasomatism (albitisation). The *inner zone* displays a pattern with no Eu anomaly and with strongly depleted HREE. Compared with Mt. Weld carbonatite carbonatites and associated REE mineralisation rocks have depleted REE abundances.

2.2 Mt Weld

The Mt. Weld carbonatite can be classified as a sövite (Le Maitre et al., 2002) because it comprises mainly calcite (>50 vol%), with subordinate apatite, phlogopite, magnetite, olivine and pyrochlore. Among four carbonatite samples from Mt. Weld examined in this study, two have porphyritic texture with phenocrysts of apatite and phlogopite in a matrix of calcite and phlogopite. The other

samples are plutonic carbonatites, exhibiting massive texture and contain abundant fresh olivine and tetraferriphlogopite. The Mt Weld sövite contains apatite, mica, magnetite, rauhaugite apatite, phlogopite, tetraferriphlogopite, pyrochlore, barite, fluorite, magnesio-arfvedsonite, galena, pyrite, sphalerite, baddeleyite, synchisite, fluocerite, monazite (Fig. 5) (Woolley and Kiarsgaard, 2008). Phlogopite phenocrysts show concentric zonation in the porphyritic carbonatites, whereas the plutonic carbonatites contain unzoned tetraferriphlogopite, and larger grains of phlogopite with occasional tetraferriphlogopite rims. Beyond calcite and phlogopite, apatite is the principal mineral in the Mt. Weld carbonatites, reaching 5-20 vol.% of the samples. It occurs as rounded or tapering long-prismatic crystals up to 900 µm in size. In the porphyritic samples, apatite displays cores overgrown by colloform rims that contain abundant calcite and phlogopite inclusions. Conversely, most apatite grains in the coarse-grained, plutonic carbonatites are unzoned. Finally, olivine grains are commonly subhedral in shape, and locally intergrown with calcite and apatite. Olivine grains are smaller than 250 µm and mainly unzoned. They occasionally exhibit an irregular rim in BSE images.



Fig. 5. Idealised cross-section of the Mount Weld carbonatite (after Pirajno, 2015).

2.3 Gifford Creek

The Gifford Creek ferrocarbonatite complex and associated alteration occupies a large area (Pirajno et al., 2014). The Gifford Creek system is considered as being part of the Warakurna Large Igneous Province (LIP), which has a very wide areal extent (Fig. 6).

2.3.1 Fenitisation

This is a type of alteration which occurs in the aureoles of carbonatites and alkaline complexes. It is essentially a desilication process accompanied by the introduction of Na, K, CO_2 , CaO and Al_2O_3 . Fenitisation is therefore characterised by the development of alkali pyroxenes (e.g. aegirine), alkali amphiboles (e.g. riebeckite), and alkali feldspars (orthoclase, microcline and albite). The latter are usually coloured red due to the presence of hematite. Affected rocks are called "fenites", derived from the Fen carbonatite where this type of alteration was first documented by Brøgger (1921). A plethora of confusing — and difficult to remember — names have been adopted by different authors to describe fenitic rocks.

Verwoerd (1967), in an attempt to solve the problem, proposed that the naming of fenitic rocks should be prefixed by the principal mineral component followed by fenite (e.g. orthoclaseaegirine-augite fenite). Fenites are formed in the country rocks surrounding the alkaline complexes, through stages of progressive metasomatism involving the elimination of free quartz and the development of alkali mineral phases. Carmichael (1974) attributed these metasomatic effects to residual alkali-rich fluids deriving from the fractionation of alkaline magmas. The fluids are in strong disequilibrium with the country rocks, resulting in haloes of alteration products which in some cases may resemble primary igneous rocks. Fenitisation is considered by many to be a solid-state transformation, due to the expulsion from the igneous complex of hot and highly reactive volatiles and their subsequent infiltration into the country rocks (Best, 1982). The spatial relationships of alkaline and carbonatite complexes, their fenitised envelopes and related mineralisation are discussed in Pirajno (2009). One of the most interesting cases of alkali metasomatism is that which takes place around alkaline complexes in stable continental areas. This phenomenon is known as fenitisation, and the



Fig. 6. The Gifford Creek ferrocarbonatite system and extent of related alteration (after Pirajno et al., 2014).

rocks affected are called fenites. The name is derived from the Fen carbonatite in Norway where this type of alteration was first documented by Brøgger (1921). A plethora of complicated names have been adopted by different authors to describe fenitic rocks.

Fenites are formed through progressive metasomatism in the country rocks surrounding alkaline complexes. This usually involves the elimination of free quartz (desilication) and the development of alkali mineral phases. Carmichael (1974) attributed these metasomatic effects to residual alkali-rich fluids deriving from the fractionation of alkaline magmas. The fluids are in strong disequilibrium with the country rocks, producing haloes of alteration products, which in some cases may resemble primary igneous rocks. The process is thought to be a solid state transformation due to expulsion from the igneous complex of hot, highly reactive volatiles and their subsequent infiltration into the country rocks (Best, 1982). The spatial relationships of alkaline and carbonatite magmas and their fenitised envelopes are illustrated in Pirajno (1992).

The composition of fenites is dependent on both the nature of the country rocks affected and the igneous complexes from which the fenitising fluids evolve. Fenitic envelopes occur mainly around carbonatites, but other alkaline complexes are also surrounded by alteration haloes with a fenitic character. Since most anorogenic alkali complexes and allied rocks occur in stable continental areas, fenite envelopes are for the greater part found within granitoids and/or basement gneisses. However, fenitisation has also been noted in basic igneous rocks and sedimentary rocks (Verwoerd, 1967; Prins, 1981). Areas affected by fenitisation may be up to 4 km from the responsible igneous intrusion. Two styles of fenitisation are recognised, one associated with carbonatites; the other with ijolites. Carbonatites form intense K-feldspar fenitisation, whereas ijolite magma is preceded by Na-K fenitisation with the production of aegirine-bearing rocks (Le Bas, 1987). Prins (1981) also concluded that K-metasomatism (feldspathisation) is associated with carbonatites, whereas Na-metasomatism (pyroxenisation) is connected with alkaline igneous rocks. The main geochemical and mineralogical features of fenitic metasomatism are described below, using primarily examples from the African continent. McKie (1962) provided a comprehensive review of the mineralogical and geochemical changes that occur during progressive fenitisation around carbonatites. In the study of the chemical changes that take place during metasomatic alteration. McKie (1962) recommended that the analyses be re-calculated in terms of cations combined with 100 anions (O, OH, F). Silica has proved to be a very useful parameter indicative of alteration (it usually, though not always, decreases with increasing fenitisation), and is therefore expedient to plot cationic values against Si variations.

A complex sequence of progressive geochemical and mineralogical changes was distinguished by McKie (1962) at Oldonyo Dili (Tanzania). Chemical changes during fenitisation show increases in Na, Fe³⁺, Ca, P, Mn and Mg and decreases in Si, with Fe²⁺, K, and AI remaining more or less constant (Pirajno, 1992). From the geochemistry of several other fenites, McKie (1962) deduced that the fenitising solutions have an oxidising character which he attributed to influx of solutions carrying Fe³⁺. Mineralogical changes took place in a granitic gneiss composed of microcline, quartz, oligoclase-albite, biotite and garnet. This sequence (Fenite 1 to 10) is summarised here. The earliest stage (Fenite 1) is characterised by strained guartz, microcline-perthite (Or94), and aggregates of magnesio-arfvedsonite replacing biotite. With advancing fenitisation (Fenite 2) guartz becomes unstrained and more common than in the original rock. Oligoclase-albite and orthoclase are abundant, and acicular aegirine inter grown with magnesio-arfvedsonite is also present (Fenite 3). In the following more advanced stages (Fenite 4) albite and aegirine, together with magnesio-arfvedsonite. are common throughout. The presence of calcite is attributed to later solutions distinct from the fenitising fluids. Marginal replacement of micro cline by orthoclase, with aegirine-forming veins and aggregates, and quartz greatly reduced, characterise the next stage (Fenite 5). Fenites 6 to 10 are essentially guartz-free. Orthoclasecryptoperthite, albite, aegirine and magnesio-arfvedsonite become the dominant minerals. Beyond Fenite 8 is the dominant orthoclase-cryptoperthite. Apatite may be locally common, and in places the orthoclase-cryptoperthite is intergrown with aegirine. The main features of the sequence of mineralogical changes described are the alteration of biotite to magnesio-arfvedsonite and aegirine, the replacement of micro cline by orthoclase and that of plagioclase by albite, and the gradual disappearance of guartz. The final product of Oldonyo Dili is a rock composed of orthoclase, aegirine with subordinate albite, magnesioarfvedsonite and apatite. The Spitzkoppe alkaline complex (South Africa) has a fenitic halo developed in granitic rocks of the Bushveld Complex. Nepheline and scapolite occur in the fenitised aureole of this complex where early investigators had difficulty in interpreting the nature of the fenitised rocks, suggesting in some cases that they may be magmatic rather than metasomatic. Verwoerd (1967), however, based on textural relationships between minerals - such as the mantling of the augites by Na-amphibole, and the intergrowths of aegirine-augite with nepheline recognised that they belong to fenitisation of the original igneous assemblages. The original composition of these rocks, whose grain size is preserved following fenitisation,

included guartz, hornblende, biotite and magnetite. These minerals reacted with fluids enriched in Na, AI, Fe³⁺, resulting in the development of aegirine and alkali amphibole at the expense of guartz and ferromagnesian minerals. Fluids containing Si, Al and Na were produced as a result of these reactions, which in turn albitised the surrounding granitic rocks over an area up to 3-4 km wide. Two types of fenite were distinguished in this area by Strauss and Truter (1950). A "red" fenite is composed of turbid microperthite, oligoclase, albite, guartz, aegirine and alkali amphibole. This fenite was later affected by a second stage of alteration in which the final products are: microcline-perthite, albite, Na-amphibole, magnetite, apatite, sphene and accessory zircon. A "white" fenite contains microc1ine-perthite, aegirine-augite, albite, sphene, apatite and magnetite, with no quartz. It is interesting to note that quartz veins present in the Bushveld granophyre within the zone of white fenite are totally replaced by albite. Prins (1981) studied the chemical changes in the fenitic aureoles of the Kalkfeld and Okorusu alkaline-carbonatite complexes (Namibia). The findings of this author - reported here - are useful to the understanding of the genesis of mineralisation and alteration connected with this type of intraplate orogenic increase, or decrease, of Si is essentially dependent on the degree of saturation in Si of the fluid relative to the invaded wall rocks. Thus, it is reasoned that if the fluids enter a Sioversaturated rock body, desilication will occur to establish equilibrium, whereas the opposite will take place if the wall rocks are undersaturated with respect to the matasomatising fluids.

The second stage of fenitisation was K-dominated and allowed the formation of orthoclase. Mass transfer equations were calculated allowing a 20% volume increase for the transformation of the pyroxene-fenite to a feldspathic fenite. Al, K and CO_3 were added, while Fe, Ti, Mg, Na, P remained constant, and Si and Ca were removed. Here feldspathisation is taken to be accompanied by desilication, because of the contrast between the invading fluid (Si-undersaturated) and the host lithology (Si-oversaturated). Silica is therefore removed but is locally re-distributed as chalcedonic breccia fillings associated with calcite. Fenitisation of mafic rocks was investigated and reviewed by Verwoerd (1967), using examples from South Africa and Namibia.

3 Mineralisation related to alkali metasomatism

Unusual concentrations of F, P, REE, Zr, Ba, Nb, Th, U, Sn, Ta and W may be present in rocks that have undergone alkali metasomatism in anorogenic ring complexes (Hou et al., 2015; Yang et al., 2019; Anenburg et al., 2021; Ma et al., 2023). These elements may form their own minerals, or they may enter the lattice of rock-forming minerals — such as tri-octahedral micas — that have crystallised in the subsolidus range of temperature and pressure. The processes that lead to the concentration of these elements are therefore linked with the action of the residual alkali-rich fluids. Their concentration either in rock-forming minerals, or in their own mineral species, is largely dependent on the original magma composition and the nature of the source rocks that have melted to produce the given magma. A review of the geochemistry and mineralisation of alkaline ring complexes can be found in a paper by Bowden (1985).

Ring complexes of the ijolite-carbonatite association may contain economic concentrations of Nb, P, F, Ba, REE and U. Good examples of this type are the carbonatite complexes in the Transvaal (South Africa) (Crocker et al., 1988), those of the Kola peninsula (Russia), Jacupiranga in Brazil, the numerous carbonatite bodies in Ontario and Quebec (Canada) and the REE orebodies of Mountain Pass in California (Hutchison, 1983). Granitic rocks, in ring complexes of the alkaline granite association (Pirajno, 1992), may contain workable concentrations of pyrochlore, columbite, cassiterite, monazite, zircon, xenotime, fluorite and REE. Pyrochlore preferentially occurs in sodic metasomatisedperalkaline granites, whereas columbite occurs in zinwaldite-albite rich granites. The anorogenic Brandberg Granite Complex in Namibia (Michael, 1989) for example. is enriched in pyrochlore in some of its marginal phases (aegirine granite). Some of the characteristic useful minerals usually associated with alkali (albite-rich) granitic rocks are given in Pirajno (2009). The anorogenic biotite granites associated with Sn ± Nb ± Ta ± W have a peralkaline chemistry, are commonly of Late Proterozoic age, and are characterised by high ⁸⁷Sr/⁸⁶Sr initial ratios (0.718 to 0.722, Hutchison, 1983). This mineralisation is well known in the Rondonia province (Brazil), in Niger, Nigeria, in the Arabian-Nubian shield and in west-central Namibia. In all cases the mineralisation appears to be related to the late phases of magmatic differentiation and the development of alkaline-rich fluids, particularly Na. Effects of albitisation can be observed at all scales, from fracture-controlled to pervasive. Albitisation processes are usually followed by, or are nearly contemporaneous with, progressively increasing stages of H⁺ metasomatism (greisenisation, Piraino, 1992). A marked separation between albitisation and subsequent greisenisation is often difficult to gauge, and hence the exact association of the mineralising fluids with one or other of the alteration phenomena not always clearcut. In broad terms it is reasonable to say that the type of mineralisation discussed here begins to take place during the postmagmatic albitisation process, and continues through, and is enhanced during, stages in which there are increasing effects from the H \sim metasomatic processes. The origin of the metals is most probably related to the source regions of the magmas. The high Sr initial ratios of the host granitic rocks suggest a crustal source. Field relationships with older stanniferous pegmatites in Namibia,

Nigeria and elsewhere (see later), indicate that this crustal source may have been already enriched in these metals.

Mineralisation in Ring Complexes of the lighte-Carbonatite Association Undersaturated alkaline ring complexes are often associated with a core of carbonatite rocks. These peculiar rocks consist largely of carbonates. At least four types are recognised (Le Bas, 1987): (1) calcite-carbonatite (coarse-grained varieties are known as sovites); (2) dolomite-carbonatite or berfosite; (3) ferrocarbonatite (ankerite-rich); (4) natrocarbonatite (mainly Na-Ca-K carbonates). Carbonatites usually occur as small plug-like bodies, or as dykes, veins, cone sheets and lavas. That they are of igneous origin is without doubt because they have been observed to occur as lava flows (eruptions of Oldoinyo Lengai in Tanzania). Bowden (pers. comm. 1988) reports that some carbonatites are not entirely magmatic, but may show metasomatic replacement features. In general, carbonatite complexes show a sequence of nephelinite through ijolite to carbonatite. The parental carbonatite magma is thought to exsolve out of a phonoliticnephelinitic melt by liquid immiscibility (Bowden, 1985). Alkali metasomatism is therefore instrumental in the production of carbonatites and their contained mineralisation. This mineralisation, however, usually evolves into epithermal systems during the late stages of the magmatic activity. Thus, processes of alkali metasomatism are followed in a continuously evolving system by hydrothermal activity with the development of low-temperature (epithermal) aqueous fluids producing vein-type mineralisation along fractures. Mineralisation in carbonatite complexes (see Batchelor and Bowden, 1985) include Ti (perovskite, ilmenite), Zr (zircon), Ba (barite), F (fluorite), P (apatite), Th and U (e.g. Urano thorianite). They can also be an important source of Al (nepheline-rich rocks) and, less commonly, Cu, Pb, Zn, Mo and Cu. Carbonatites are also enriched in LREE (light rare earth minerals). There are, according to Bowden (1985), two main associations: apatite-magnetite usually related to sovites and also containing pyrochlore, and REE association with late-stage enrichments of barite, usually found in ankeritic rocks, without magnetite and pyrochlore. Some good examples of carbonatite complex-related mineralisation can be found in South Africa (see Table 4.3 in Pirajno, 2009) and are briefly reviewed below: Activity that resulted in the development of hydrothermal convection cells and the deposition of quartz vein material, with open space fillings of barite, fluorite and sulphide mineralisation. No apatite is present in this type of mineralisation. It is, incidentally, of interest to note that some of these deposits are also being investigated for possible epithermal-type Au mineralisation. The Pilanesberg Complex, which intrudes the western lobe of the Bushveld Igneous Complex, consists of a central zone of white and red foyaite, surrounded by concentric zones of lavas and pyroclastics, followed by a ring of red syenite. Within the Complex there are more than

a dozen mineral occurrences, one of which is the Whydhoek deposit containing fluorite and apatite. This mineralisation is associated with coarse-grained (pegmatitic) Kfeldspar and aegirine, and is contained in a cylindrical zone developed at the contact between pyroclastics and the red foyaite. In one place the ore is distinctly zoned with an inner fluorite-apatite-aegirine assemblage and an outer pegmatitic apatite-aegirine assemblage. The ore is composed of approximately 40-60% fluorite and 20-30% apatite, with traces of sulphides. In other places fluorite can be seen to occur as an interstitial constituent between the laths of orthoclase in coarse-grained foyaite. Based on textural evidence, Crocker et al. (1988) consider that the fluorite may have crystallised from a low temperature magmatic melt. Mineralisation of the fluorite-apatite-carbonate association is present at several localities. This mineralisation is characterised by lenses, stringers, veinlets and breccia dykes (or tuffisites, thought to be the result of gas streaming). Carbonate minerals are dolomite and calcite. The Pilanesberg Complex also contains REE mineralisation in the form of the primary mineral britholite. This mineralisation occurs in veins along the contact between a tinguaite ring dyke and a foyaite. The latter also contains disseminated ore. Analysis of concentrates gave 58% of REE oxides (mainly Ce, La, Nd and Pr) (Coetzee, 1976).

The Pienaars River Complex is formed by trachytic rocks, various pyroclastic units, syenites, foyaites, phonolites and some minor carbonatite. These rocks are subdivided into three suites, namely: Roodeplaat, Leeuwfontein and Franspoort. Several mineral occurrences are present mostly within the trachytic rocks. At one locality (Wallmannsthal) the mineralisation consists of intergrown fluorite and apatite with minor disseminated pyrite and chalcopyrite; at another, lenses of fluorite-apatite mineralisations are present. They are associated with an intrusive foyaite plug emplaced into a quartzite, which as a result was brecciated and alkali-metasomatised with development of orthoclase laths. The fluorite-apatite mineralisation occurs as interstitial grains and clusters up to a few centimetres in size, within the foyaitic rock, which is composed of orthoclase and nepheline set in a matrix of feldspars and amphiboles. In the quartzite rock the fluorite-apatite occurs along the edges of the brecciated fragments.

The Kruidfontein Carbonatite Complex was intruded into dolomitic rocks of the Transvaal sequence. It is a ring structure consisting of an outer zone made up of trachytic, rhyolitic, basaltic and pyroclastic rocks, and an inner zone made up of massive metaberfosite surrounded by a ring of "bedded" metaberfosite and sovite bodies. Crocker et al. (1988) interpreted the inner carbonatitic rocks as having originated by metasomatic replacement of pre-existing rocks (mainly pyroclastics), The Palabora mineralisation (see Pirajno, 2009 for an overview and references therein) consists of Cu with minor magnetite uranothorianite and

baddeleyite (ZrO₂) with traces of Hf, all of which are extracted from the central Lolekop carbonatite complex. Apatite and vermiculite are also mined. The Cu mineralisation occurs disseminated within the foscorite, which forms the dyke-like core of the carbonatite. Copper mineralisation is represented by chalcopyrite and bornite, with minor cubanite, pyrrhotite and other sulphides of Cu, Pb, Co and Zn. Vallereite is also present as a late-stage phase, mainly along shear zones crosscutting the ore body. Apatite occurs within the phlogopite-bearing pyroxenite, while magnetite forms up to 50% of the foscorite and is invariably titaniferous and zoned around the Cu mineralisation.

The formation of carbonatites and their associated REE mineralization is fundamentally driven by multi-stage evolution (Xie et al., 2015; Smith et al., 2016; Anenburg et al., 2021). Radiogenic isotopic compositions of carbonatite-associated REE deposits suggest an origin from enriched mantle, which were previously metasomatism by different component (e.g., subduction-derived component) (Hou et al., 2015; Zhao et al., 2025). A model explains the source of these REE-bearing carbonatite by metasomatism of the subcontinental lithospheric mantle (SCLM) by REE-rich fluids/melts derived from subducted plate. REE-enriched metasomatized mantle is then available for subsequent melting events, which lead to crustal formation of REE deposits (Hou et al., 2023).

Carbonatite magmas are either immiscible from silicate melts, or directly the mantle derived melts, or extensive fractional crystallisation of a carbonate-silicate parent melts. The majority of REE-enriched carbonatite magmas are widely interpreted to originate through melts immiscibility processes from coexisting silicate melts (Brooker and Kjarsgaard, 2011; Veksler et al., 2012; Martin et al., 2013; Nabyl et al., 2020). The immiscibility-driven origin has been are supported by field evidences of carbonatite and alkaline magma spatial associations (Woolley, 1987; Kjarsgaard and Hamilton, 1989), and experimental surveys (Brooker and Kjarsgaard, 2011; Veksler et al., 2012; Martin et al., 2013; Nabyl et al., 2020). Experimental simulation shows that REE preferentially partitions in the carbonatitic magma as crystal fractionation proceeds of alkaline silicate magmas (Nabyl et al., 2020). Highly fractionated crystallization process can be enriched in REE in residual carbonatite magma (Nabyl et al., 2020). Subsequently, carbonatite magmas typically first crystallise calcite, followed by dolomite, then Fe-rich dolomite or ankerite. REE is strongly enriched in the liquid owing to their incompatibility in Ca-, Mg-, Fe-, carbonate (Chebotarev et al., 2022). In the magmatic-hydrothermal system or the end evolution stage of carbonatite, Fractional crystallization and the magmatichydrothermal transitions enhance the massive enrichment of REE in systems. Fractional crystallization of carbonate minerals and immiscibility of melts and hydrothermal fluids in the hydrothermal evolution stage play an important role

in upgrading the REE mineralization. Finally, REE minerals precipitation in and around carbonatites though changes of temperature, pressure, pH and composition of the fluids or melts, accompanying by the occurrence of alkaline meta-somatism in the wall rock (Xie et al., 2015; Anenburg et al., 2020; Mororó et al., 2024).

4 Conclusions

Carbonatites and associated REE minerals have a significant role in modern technology. They have important roles in energy efficiency, such as fluorescent lights, hybrid vehicles, wind turbines, and digital technology such as flat panel displays and digital cameras, to mention a few. REE mineral systems occur as primary bastnaesite, monazite in calcic-carbonatite, ferrocarbonatite and in hydrothermal deposits as veins, breccias and fenites. Carbonatites are associated with rift-related magmas in continental Large Igneous Provinces.

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Declaration of competing interest

The corresponding author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit Author statement

Franco Pirajno: Conceptualization; Data curation; Formal analysis; Visualization; Writing—original draft; review & editing.

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