

Multi-stage formation of REE minerals in the Palabora Carbonatite Complex, South Africa

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ABSTRACT

The 2060 Ma old Palabora Carbonatite Complex (PCC), South Africa, comprises diverse REE mineral assemblages formed during different stages and reflects an outstanding instance to understand the evolution of a carbonatite-related REE mineralization from orthomagmatic to late-magmatic stages and their secondary post-magmatic overprint. The 10 rare earth element minerals monazite, REE-F-carbonates (bastnäsite, parisite, synchysite), ancylite, britholite, cordylite, fergusonite, REE-Ti-betafite, and anzaite are texturally described and related to the evolutionary stages of the PCC. The identification of the latter five REE minerals during this study represents their first described occurrences in the PCC as well as in a carbonatite complex in South Africa.

The variable REE mineral assemblages reflect a multi-stage origin: (1) fergusonite and REE-Ti-betafite occur as inclusions in primary magnetite. Bastnäsite is enclosed in primary calcite and dolomite. These three REE minerals are interpreted as orthomagmatic crystallization products. (2) The most common REE minerals are monazite replacing primary apatite, and britholite texturally related to the serpentinization of forsterite or the replacement of forsterite by chondrodite. Textural relationships suggest that these two REE-minerals precipitated from internally derived late-magmatic to hydrothermal fluids. Their presence seems to be locally controlled by favorable chemical conditions (e.g., presence of precursor minerals that contributed the necessary anions and/or cations for their formation). (3) Late-stage (post-magmatic) REE minerals include ancylite and cordylite replacing primary magmatic REE-Sr-carbonates, anzaite associated with the dissolution of ilmenite, and secondary REE-F-carbonates. The formation of these post-magmatic REE minerals depends on the local availability of a fluid, whose composition is at least partly controlled by the dissolution of primary minerals (e.g., REE-fluorocarbonates).

This multi-stage REE mineralization reflects the interplay of magmatic differentiation, destabilization of early magmatic minerals during subsequent evolutionary stages of the carbonatitic system, and late-stage fluid-induced remobilization and re-/precipitation of precursor REE minerals. Based on our findings, the Palabora Carbonatite Complex experienced at least two successive stages of intense fluid–rock interaction.

Keywords: Rare earth minerals, Loolekop, monazite, britholite, anzaite, fluoro-carbonates, ancylite, cordylite, fergusonite, REE-Ti-betafite

INTRODUCTION

Carbonatites are important exploration targets for rare earth elements (REE) and high field strength elements (HFSE, e.g., Mariano 1989; Wall and Mariano 1996; Verplanck et al. 2016). Since REE have become increasingly important for industrial use (Chakhmouradian and Wall 2012; Hatch 2012; Wall 2014) and were categorized as critical and strategic metals (European Commission 2014; Nassar et al. 2015), the scientific interest to understand the complex REE mineralizations found in carbonatitic systems has tremendously increased (e.g., Verplanck et al. 2016). Processes potentially responsible for REE enrichment

in carbonatites include fractional crystallization of carbonatitic magma, enrichment of REE in magmatic fluids and subsequent precipitation, breakdown of primary carbonatitic minerals with sequestration of REE in secondary minerals, and subsolidus redistribution of REE (e.g., Verplanck et al. 2016). In all these processes, REE-bearing minerals (such as apatite, calcite, and dolomite) have to be distinguished from actual REE minerals with REE as major constituents. The most common REE minerals in carbonatites include REE-phosphates (mostly monazite) and various hydrous and anhydrous carbonates (e.g., ancylite, burbankite, and carbocearnite) and fluorocarbonates, such as bastnäsite, parisite, and synchysite (e.g., Wall and Zaitsev 2004b; Kanazawa and Kamitani 2006).

This study presents detailed textural observations on the vari-

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ous REE phases in the Loolekop pipe of the Palabora Complex (PCC, South Africa). These textural relations to both the carbonatitic minerals and among each other are used to distinguish between orthomagmatic, late-magmatic, and post-magmatic stages of formation and provide a better understanding for the importance of fluid-assisted mobilization and reprecipitation of these minerals. Understanding these typically late-stage processes is crucial for any economic judgement on REE in carbonatites (Wall and Zaitsev 2004a; Chakhmouradian and Zaitsev 2012; Zaitsev et al. 2015). Accordingly, the aim of this study is to present the crystallization and alteration history of the various REE minerals within the different evolutionary stages observed in the PCC as a prime example of REE-mineralized, large carbonatitic systems worldwide.

GEOLOGICAL BACKGROUND AND PREVIOUS WORK ON THE REE MINERALIZATION AT PALABORA

The Palabora Carbonatite Complex (PCC) is located close to the town of Phalaborwa (South Africa) and intruded at about 2060 Ma into Archaean basement rocks (Reischmann 1995; Wingate and Compston 2000; Heaman 2009; Wu et al. 2011). The complex represents an elongated tripartite pipe-like intru-

sion divided into a northern and southern pyroxenite and the central Loolekop pipe, with only the latter hosting carbonatites (Fig. 1; Hanekom et al. 1965; Yuhara et al. 2003; Verwoerd and Du Toit 2006).

The Loolekop pipe is composed of phoscorite (FOS) and banded carbonatite (BCB), which are intruded by transgressive carbonatite (TCB). Both the BCB and TCB are dolomite-bearing, but calcite-dominated with varying proportions of fluorapatite, phlogopite, magnetite, forsterite/chondrodite, and accessory phases (Fig. 2). Geochronological data indicate no significant age differences between these two rock types and Wu et al. (2011) suggest that they crystallized from different magma batches derived from a heterogeneous mantle source. Subsequent injection of a sulfide-rich liquid caused Fe-Cu-sulfide enrichment in the carbonatite pipe (Kavecsanszki et al. 2012). The carbonatite-phoscorite association is surrounded by micaceous pyroxenite (MPY, Lombaard et al. 1964; Hanekom et al. 1965; Eriksson 1989). Several syenite bodies were injected into the surrounding basement rocks in the vicinity of the complex (Eriksson 1989; Yuhara et al. 2003; Wu et al. 2011) and the basement rocks in the border zone toward the complex were fenitized (Verwoerd 1966). The entire complex was cross cut by dolerite dikes (DOL),

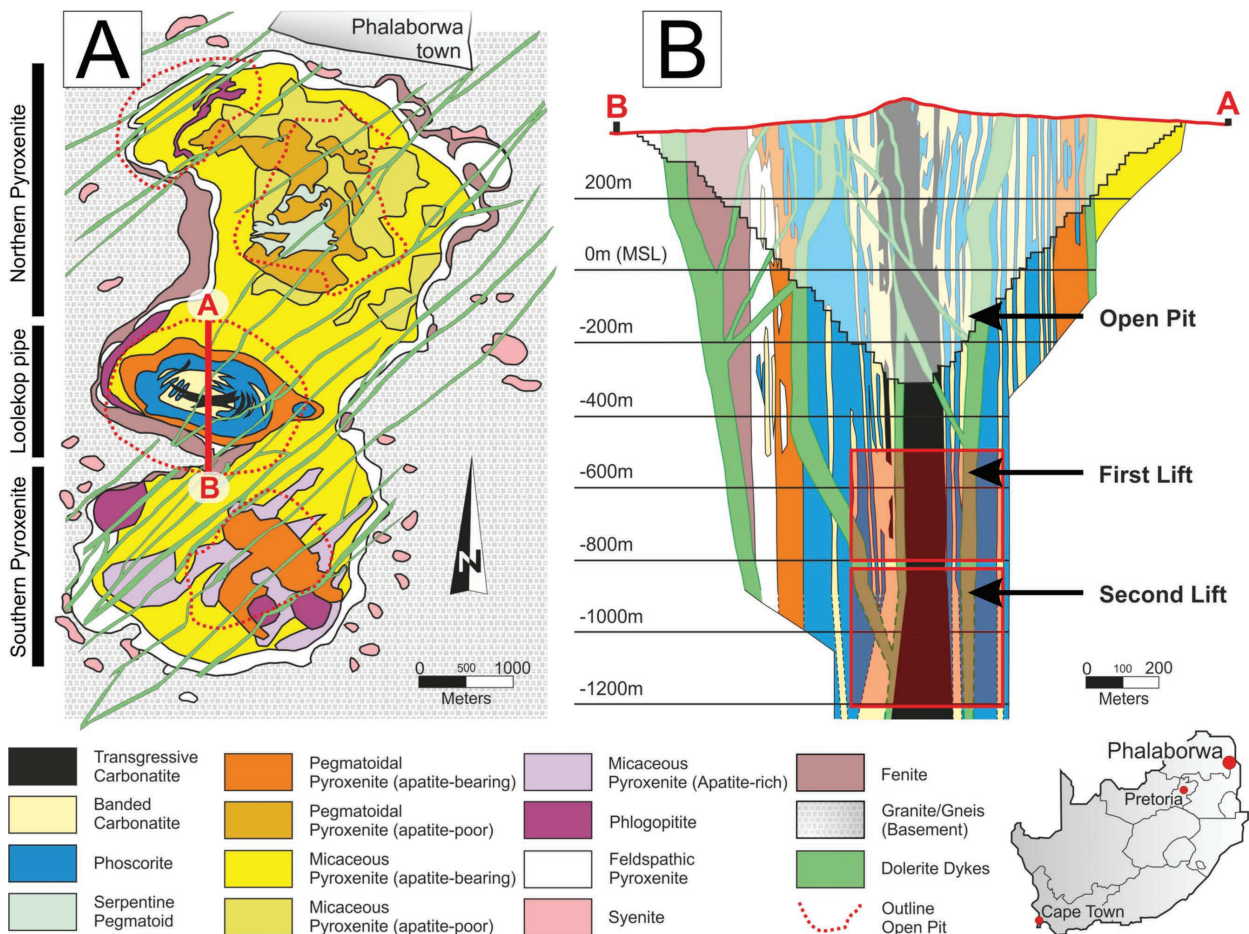
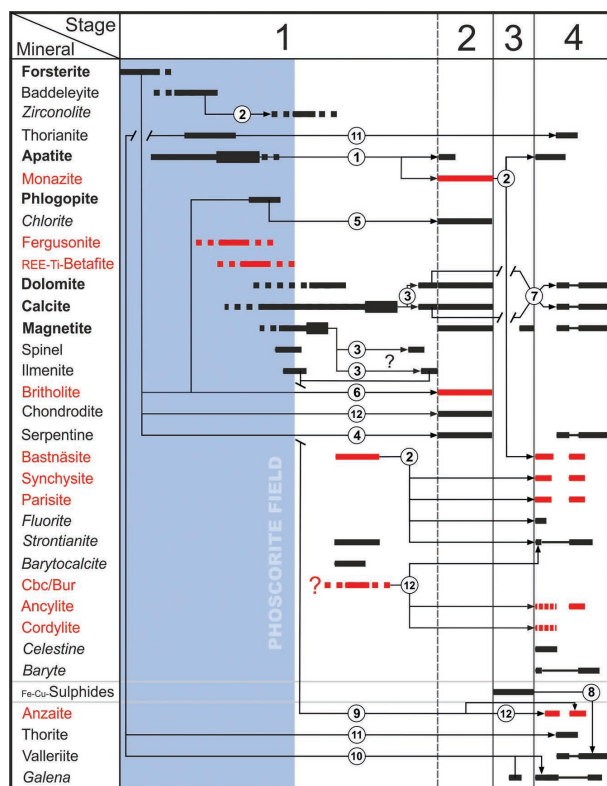


FIGURE 1. Generalized geological map of the Palabora Complex (modified after Hanekom et al. 1965; Fourie and De Jager 1986; Wilson 1998) and cross section of the Loolekop pipe in N-S direction showing the irregular ring structure of the pipe (modified and extended after Wilson 1998).



Stage of mineral formation:

(1) Ortho-Magmatic Stage (2) Late-Magmatic Stage
(3) Sulphide Stage (4) Post-Magmatic Stage

① Redistribution of P ② Alteration ③ Exsolution ④ Serpentinization
⑤ Chloritization ⑥ Redistribution of Si ⑦ Recrystallization
⑧ Valleritization ⑨ Redistribution of Ti ⑩ Redistribution of Pb
⑪ Redistribution of Th ⑫ Replacement

FIGURE 2. Paragenetic scheme for carbonatites and phoscorite (blue field) of the Loolekop deposit. Note: Main phases in bold, minor phases in plain style, accessory phases in italics, and REE phases in red.

which were interpreted as being Proterozoic (Briden 1976; Stettler et al. 1989; Wu et al. 2011) to Post-Karoo (<180 Ma) in age (Hanekom et al. 1965; Uken and Watkeys 1997).

Very similar to what is observed in other carbonatite complexes, apatite represents the main REE host in carbonatites from the PCC and is much higher in REE than calcite and dolomite (Dawson and Hinton 2003). Early investigations on the REE distribution in carbonatites of the PCC suggested the absence of REE minerals (Aldous 1980). Later, bastnäsite, parisite, synchysite, ancyrite, monazite, Sr-REE apatite, and an unknown REE-silicate were described by Bulakh et al. (1998) and Karchevsky (2000). These studies used the same five samples from the open pit level (random sampling—upper 600 m of the deposit; Bulakh, personal communication) and provided only incomplete textural descriptions on their occurrence. Bastnäsite (and minor parisite) was identified as the most abundant REE mineral in the BCB, whereas ancyrite (and minor synchysite) was described as the most abundant REE mineral in the TCB. Monazite was described as mainly forming rims around or veins

in apatite and an unknown REE-silicate was mentioned to form rims around chondrodite.

SAMPLE MATERIAL AND ANALYTICAL METHODS

The Loolekop pipe is divided into three sections: the open pit level (uppermost part), the first lift level (upper underground level), and the second lift level (lowest part, Fig. 1), representing a vertical profile of >1500 m. We collected about 400 samples from 6 drill holes (LK-109, U-2, U-33, MT-1, SL-131, FS-14) and the observations reported in the following derive from 45 representative samples (20 TCB, 15 BCB, and 10 FOS) covering all three levels of the Loolekop pipe. All mineral formulas and abbreviations used are given in Table 1.

Polished thin sections were investigated using petrographic and reflected-light microscopes and were further examined using the backscattered electron (BSE) mode (focused beam) of a Hitachi Tabletop SEM (Tübingen), a JEOL JSM-6610 SEM (UFS, Bloemfontein), and the FE-SEM of the Centre for Microscopy (UFS, Bloemfontein).

Quantitative analyses of REE minerals were acquired using a JEOL JXA 8230 Superprobe at the Department of Geology, Rhodes University and a JEOL JXA 8900 Superprobe at the Department of Geosciences, Eberhard Karls University, Tübingen. Data acquisition was performed using four wavelength-dispersive spectrometers. Standardization was done using natural mineral standards, synthetic REE phosphates (SPI Supply), and REE1-4 glasses (Drake and Weill 1972). The ZAF matrix correction method (Bence and Albee 1968; Armstrong 1988) was employed for quantification, except for monazite, where a PRZ (JEOL) correction was used. For analyses of the different REE minerals, variable settings were used as detailed in the electronic appendix¹.

RESULTS

Crystallization sequence of the Palabora carbonatites and phoscorites

Here we provide an overview of the crystallization sequence for carbonatites and phoscorites of the Loolekop deposit. Detailed descriptions of REE minerals (marked red in Fig. 2) are given in the subsequent chapter. The PCC experienced at least four stages of crystallization, which were distinguished as (1) orthomagmatic, (2) late-magmatic, (3) sulfide-rich, and (4) post-magmatic. Phoscorites (blue field in Fig. 2) are dominated by orthomagmatic minerals, whereas in carbonatites later-magmatic minerals are more common. Although BCB and TCB were classified as two different carbonatites (e.g., Wu et al. 2011), they show some textural differences (from fine banding of mainly magnetite, apatite, and phlogopite in BCB to large patchy crystallization of the same minerals in TCB) but generally comprise the same mineral assemblages in the same crystallization sequence. This favors integration into a single paragenetic scheme together with the phoscorites (Fig. 2).

The orthomagmatic crystallization (stage 1) commenced by the formation of forsterite (with higher abundance in BCB), apatite, baddeleyite (later altered to zirconolite), and thorianite (Figs. 3a–3e). Subsequent formation of phlogopite (with higher abundance in BCB; Figs. 3d–3f) is followed by magnetite (with minor spinel and ilmenite; Figs. 3g and 3h), which exsolved further spinel (Figs. 3i and 3j) and ilmenite (Figs. 3i–3k) during later cooling. Precipitation of Mg-rich calcite started during the final stages of apatite formation with its main crystallization phase outlasting that of magnetite. A dolomite formation stage (Fig. 3l) existed contemporaneous with the intermediate stages of calcite formation, and during the main calcite stage,

¹Deposit item AM-17-66004, Supplemental Material and Table 2. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2017/Jun2017_data/Jun2017_data.html).

TABLE 1. Chemical formulae of the minerals mentioned in the text and figures

Mineral	Abbr.	Formula	Mineral	Abbr.	Formula
SILICATES:			CARBONATES:		
chlorite	chl	$(\text{Mg},\text{Al}_2\text{Si}_2\text{Al})\text{O}_{10}(\text{OH})_8$	ancylite-(Ce)	anc	$(\text{Sr,Ca})(\text{REE})(\text{CO}_3)_2(\text{OH})\cdot\text{H}_2\text{O}$
chondrodite	chn	$(\text{Mg},\text{Fe})_2(\text{SiO}_4)_2(\text{F},\text{OH})_2$	bastnäsite-(Ce)	bsn	$(\text{REE,Ca})(\text{CO}_3)_2\text{F}$
fluorbritholite-(Ce)	bri	$\text{Ca}_2(\text{REE})_3(\text{SiO}_4)_3(\text{F},\text{OH})$	burbankite	bur	$(\text{Ca},\text{Na})_3(\text{Sr,REE,Ba})_3(\text{CO}_3)_5$
olivine	ol	$(\text{Mg},\text{Fe})\text{SiO}_4$	calcite	cal	CaCO_3
phlogopite	phl	$\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2$	carbocernaite	cbc	$(\text{Ca},\text{Na})(\text{Sr,REE,Ba})(\text{CO}_3)_2$
serpentine	srp	$\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	cordylite-(Ce)	cdy	$(\text{Ca},\text{Na})\text{Ba}(\text{REE})_2(\text{CO}_3)_3\text{F}_2$
thorite	thr	ThSiO_4	dolomite	dol	$\text{CaMg}(\text{CO}_3)_2$
OXIDES:			parisite-(Ce)	pst	$\text{Ca}(\text{REE})_2(\text{CO}_3)_3\text{F}_2$
anazaite-(Ce)	anz	$(\text{REE})_4\text{FeTi}_6\text{O}_{18}(\text{OH},\text{F})_2$	strontianite	str	$(\text{Sr,Ca,Ba})\text{CO}_3$
baddelyite	bdl	ZrO_2	synchysisite-(Ce)	syn	$\text{Ca}(\text{REE})(\text{CO}_3)_2\text{F}$
REE-Ti-betafite-(Ce)	btf	$(\text{REE,Ca})_2\text{Ti}_2\text{O}_6(\text{O},\text{OH},\text{F})$	barytocalcite	bcl	$\text{BaCa}(\text{CO}_3)_2$
fergusonite-(Nd)-β	frg	$(\text{REE})\text{NbO}_4$	SULFATES:		
ilmenite	ilm	FeTiO_3	baryte	brt	BaSO_4
magnetite	mgt	Fe_3O_4	celestine	cls	SrSO_4
spinel	spl	MgAl_2O_4	PHOSPHATES:		
thorianite	thn	ThO_2	fluorapatite	ap	$\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH})$
zirconolite	zrc	$\text{CaZrTi}_2\text{O}_7$	monazite-(Ce)	mnz	$(\text{REE,Ca})\text{PO}_4$
SULFIDES:			HALIDES:		
bornite	bn	Cu_5FeS_4	fluorite	fl	CaF_2
chalcopyrite	cp	CuFeS_2			
galena	gn	PbS			
valleriite	val	$2[(\text{Fe,Cu,S})\cdot 1.53[(\text{Mg,Al})(\text{OH})_2]]$			

additional Sr- and Ba-carbonates formed. Exsolution of dolomite and Mg-poor calcite from Mg-rich calcite (Fig. 3m) concludes the magmatic stage 1.

A late-magmatic stage (stage 2) is reflected by the serpentinization (and further magnetite formation) of forsterite (Figs. 4e and 4f) and replacement of forsterite by chondrodite (Fig. 4g), occasional chloritization of phlogopite (Figs. 4h), and the formation of secondary apatite (ap-II). Stage 2 interweaved with stage 1 and is probably the result of the action of aqueous-carbonic fluids (LM fluid in the following).

The subsequent injection of a sulfide-rich liquid (stage 3) resulted in extensive Fe-Cu sulfide mineralization (with minor magnetite). The interaction of a sulfide magma with the carbonatite magma is suspected during this stage (Kavecsanszki et al. 2012).

Subsequently, a post-magmatic fluid (stage 4; PM fluid in the following) caused a second serpentinization event (again associated with magnetite), valleriitization of the sulfide minerals (Figs. 4c, 4d, and 5e), recrystallization of carbonates (Fig. 6g; restricted to TCB), and the formation of thorianite, thorite (Figs. 6g and 6h; restricted to TCB), galena, baryte, celestine (Fig. 7f), and late-stage apatite (ap-III; Figs. 6f and 5f).

Textural appearance of REE minerals in the Palabora carbonatites and phoscorites

Ten REE minerals were identified during this study (marked red in Fig. 2; plus the suspected former occurrence of carbocernaite/burbankite), partly occurring in different generations. All REE minerals from the PCC are strongly LREE-enriched (Table¹ 2) and typically represent Ce-dominated members, which is displayed by the suffix-(Ce) after the nomenclature of Bayliss and Levinson (1988). The only exception is fergusonite, which reflects a Nd-rich end-member [fergusonite-(Nd)-β]. Even though the suffix use in the mineral nomenclature is recommended by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA), for simplification we abstain from using the suffix in the following.

Fergusonite. The REE-niobate fergusonite (Table¹ 2) at the

PCC belongs to the Ce-enriched, Nd-dominated end-member of this mineral group and is very rare compared to all other REE minerals found in the Palabora carbonatites. It mostly occurs as rounded to irregular inclusions (max. 80 μm) in magnetite, often associated with baddelyite and zirconolite (Figs. 8a and 8b).

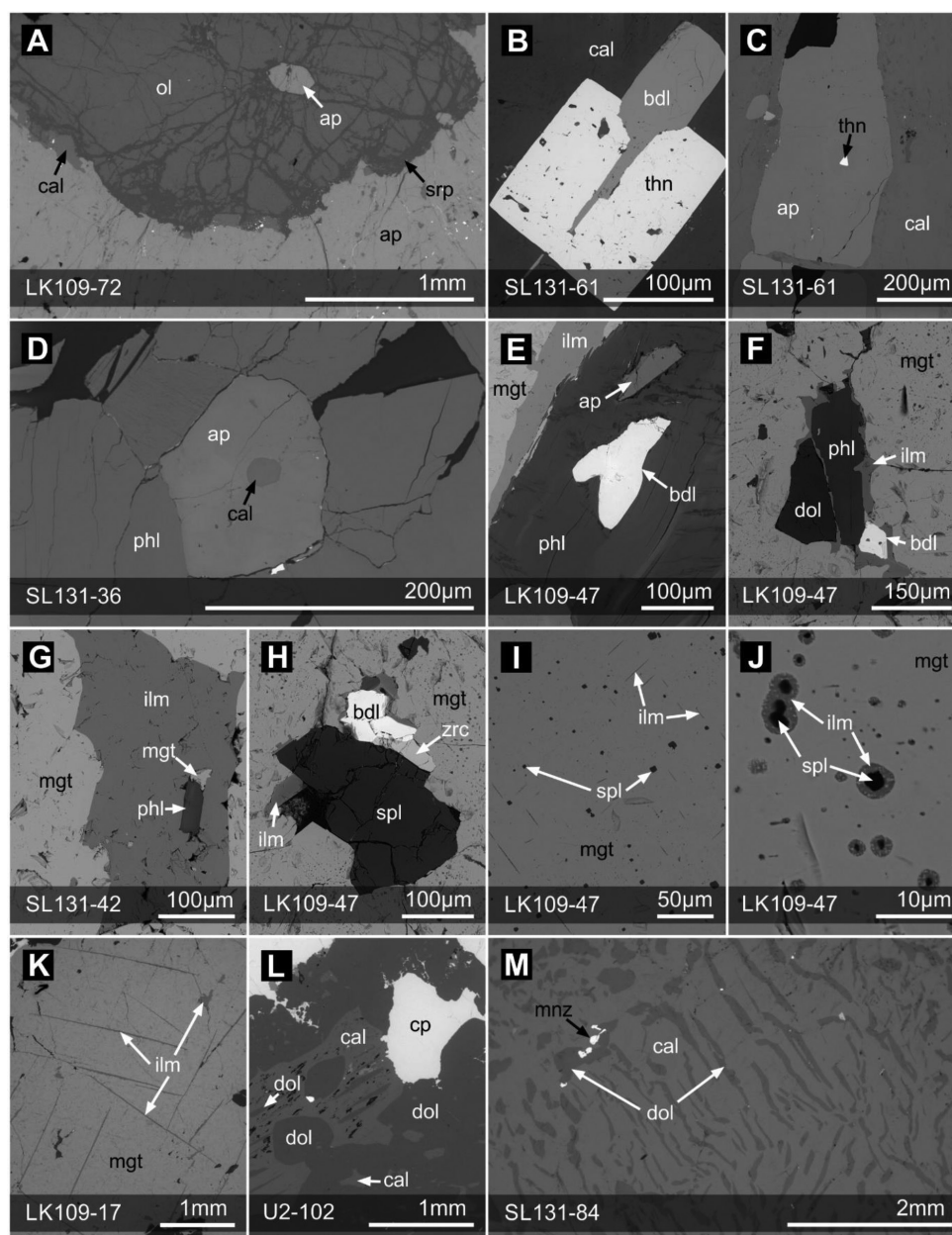
REE-Ti-betafite (pyrochlore-group member). The REE-Ti-oxide REE-Ti-betafite (alternatively named ceriobetafite; not approved by IMA; Table¹ 2) seems to be restricted to TCB and represents, after fergusonite, the second rarest REE mineral in the PCC. Betafite requires Ti/(Nb+Ta+Ti) ratios above 1/3. Compositions with Ti > Nb+Ta (Ti-betafite) are very rare and normally exclusively known from granite pegmatites (Yaroshevskii and Bagdasarov 2008). REE-Ti-betafite in the PCC occurs as 25–75 μm sized needles and rods, mostly as inclusions in magnetite or, more rarely, in dolomite and calcite (Figs. 8c and 8d).

REE-F-carbonates. The REE-fluorocarbonates bastnäsite, parisite, and synchysisite (Table¹ 2) are strongly associated with each other, with bastnäsite being by far the most abundant (>80% of all measured REE-F-carbonates). The following three associations can be distinguished.

The first type (REEFC-I) occurs mostly as 10–200 μm sized rods enclosed in magmatic calcite and dolomite (Figs. 6a–6c) and is associated with fluorite, strontianite (Fig. 6d), or ancylite (see below). These rods are often partly dissolved and form optically continuous single crystals (Figs. 6a–6d). REEFC-I needles partly included in sulfides show a higher resistance to dissolution for parts protected by the sulfide phase (Fig. 6b). The second type (REEFC-II a; restricted to TCB) forms as bastnäsite rods in the vicinity of monazite replacing apatite and is mostly associated with sulfides, valleriite, and ap-III (Figs. 6e and 6f). A third type (REEFC-II b; restricted to TCB) consists mainly of bastnäsite and generally occurs as irregularly shaped grains (5–100 μm) in late-stage carbonate veins (Figs. 6g and 6h). This type is frequently intergrown with magnetite or strontianite and contains inclusions of thorianite and rarely thorite (Figs. 6g and 6h). In few cases REEFC-II b is associated with anazaite (Fig. 6h).

Monazite. The REE-phosphate monazite (Table¹ 2) typically

FIGURE 3. General orthomagmatic mineral assemblages observed in carbonatites and phosphorite from the Looelekop deposit. (a) Euhedral apatite inclusion in partly serpentinized forsterite. (b) Intergrowth of magmatic baddeleyite and thorianite. (c) Euhedral inclusion of thorianite in apatite. (d) Calcite inclusion in apatite, which again is enclosed in phlogopite. (e) Baddeleyite and apatite inclusions in phlogopite. (f) Dolomite and phlogopite surrounded by ilmenite in magnetite. Baddeleyite included in ilmenite. (g) Ilmenite with inclusions of phlogopite and magnetite, all included in magnetite. (h) Spinel with baddeleyite and zirconolite included in magnetite. (i) Exsolved spinel cubes (note the equality of orientation) associated with exsolved ilmenite lamellae in magnetite. (j) Slightly rounded spinel with a rim of ilmenite in magnetite. (k) Ilmenite exsolution lamellae in magnetite. (l) Distinct dolomite accumulations partly enclosed in calcite with dolomite exsolution (arrow). (m) Sub-graphic intergrowth of vermicular dolomite exsolutions with calcite.



represents La-enriched, Ce-dominated monazite [lanthanian monazite-(Ce) after the nomenclature of Bayliss and Levinson 1988]. Monazite is almost always replacing apatite, forming thin skins ($\geq 3 \mu\text{m}$) to massive rims ($\leq 40 \mu\text{m}$) around the latter (Fig. 4a). These textures can develop to a nearly complete replacement of apatite with lobate-like expansions up to 300 μm in diameter (Fig. 4a). In some cases relics of apatite are surrounded by thick rims of monazite (40–300 μm) in cases together with calcite (Fig. 4b). More uncommon appearances include monazite enclosed or in contact with sulfides, which may show reaction rims toward apatite in contact to the reaction of primary sulfide to vallerite (Figs. 4c and 4d).

Britholite. The Ca-REE-silicate britholite (Table 2) is mainly present as fluorbritholite-(Ce). Britholite forms rims ($\leq 60 \mu\text{m}$

thick) around forsterite-serpentine/chondrodite assemblages, where it usually precipitates at the outer rim of the serpentine (Figs. 4e and 4f) and chondrodite (Fig. 4g). In rare cases britholite ($\sim 20 \mu\text{m}$ thick) is also found in contact with phlogopite/chlorite (Fig. 4h).

Ancylite. The hydrous REE-Sr-carbonate ancylite (Table 2) occurs in two textural varieties: The first type (ANC-I) forms 15–100 μm sized needles, rods, or irregular grains (Figs. 7a–7c) that may contain tiny inclusions of baryte (Figs. 7a and 7b) and are enclosed in calcite and dolomite (in cases associated with REEFC-I). ANC-I is often associated with strontianite and cordylite (see below). A second type (ANC-II) is restricted to TCB and forms 10–50 μm sized grains that are mostly associated with magnetite, thorite (Figs. 7d and 7e), strontianite, and baryte

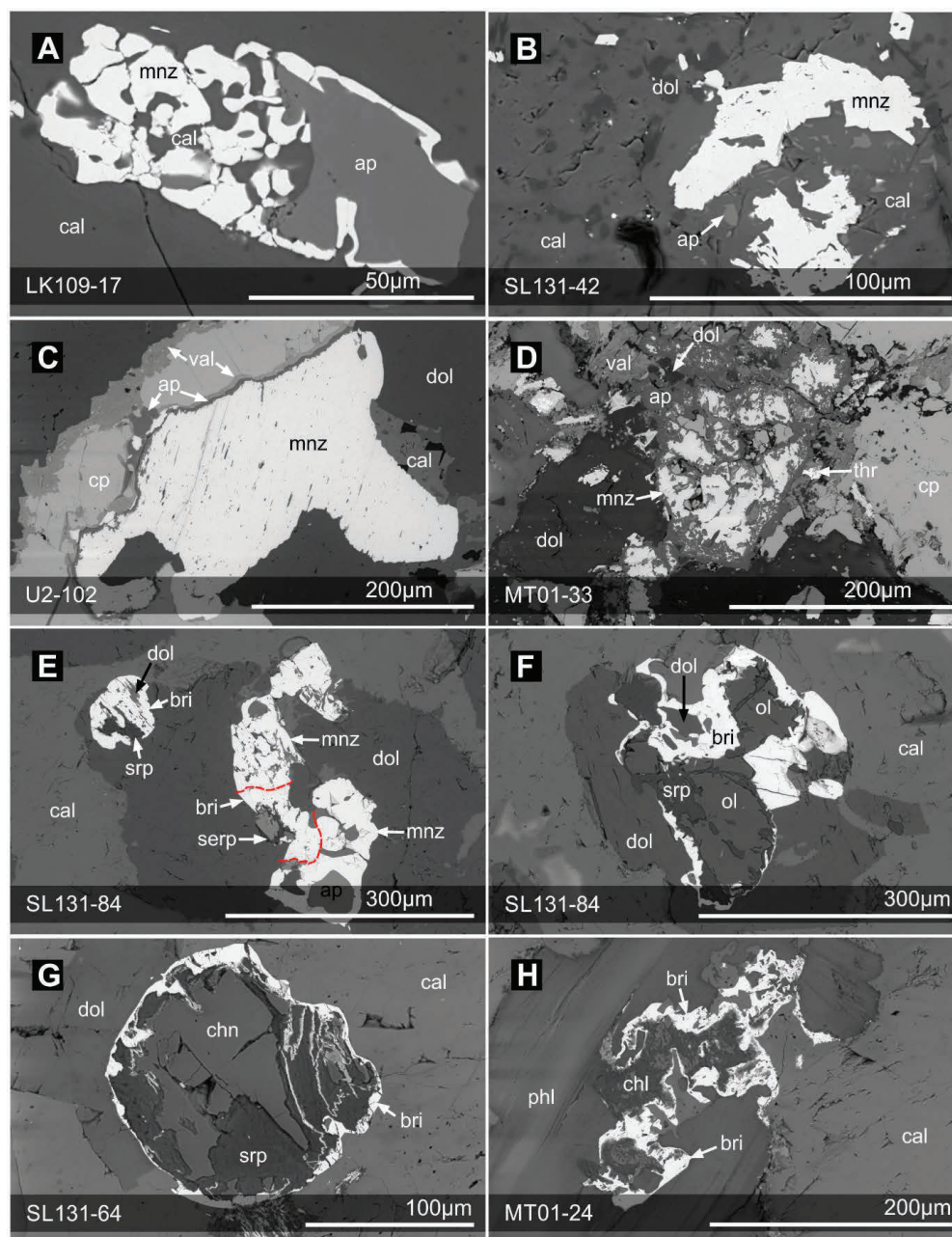


FIGURE 4. Textural appearances of monazite and britholite. (a) Lobate-like expansions of monazite rim around apatite. (b) Tiny relics of apatite enclosed by calcite with a thick rim and irregular precipitation of monazite. (c) Monazite partly enclosed by sulfides with apatite rim where sulfide shows valleriitization. Note the lack of apatite rim at monazite where no valleriitization took place. (d) Strongly altered monazite with formation of secondary apatite associated with valleriitization of sulfides. Note thorite inclusions in valleriite. (e) Monazite and britholite in equilibrium around serpentinized forsterite and apatite. The red dashed line marks the border between britholite and monazite. (f) Thick britholite rim around monazite. (g) Britholite around forsterite replaced by chondrodite and serpentine. (h) Britholite associated with phlogopite and chlorite.

and rarely occur as crack-fillings together with magnetite and celestine (Fig. 7f). Similar to REEFC-II b, this type occurs in late carbonate veins, but shows a higher affinity to serpentine, where REE-F-carbonates are usually absent (Figs. 7d and 7e).

Cordylite. Similar to ANC-I, the REE-Ba-carbonate cordylite (Table 2) occurs as 10–100 µm sized needles or irregular

grains enclosed in calcite and dolomite (Figs. 7g and 7h). Cordylite is often patchy (Fig. 7h) and may show tails filling tiny veins (Fig. 7g). It was only found in few samples mainly from the uppermost part of the Loolekop pipe, where baryte and celestine are relatively abundant. Importantly, cordylite in the direct vicinity of partly dissolved REEFC-I (see above)

shows no dissolution or alteration features.

Anzaite. A REE-Ti-oxide rarely found in the PCC is most likely anzaite (Table 2), which up to now has only been described from the Afrikanda Complex (Russia; Chakhmouradian et al. 2015). To ultimately distinguish anzaite from a cation-deficient perovskite (which has to date not been described from a natural occurrence, though) XRD analyses would be needed (Chakhmouradian et al. 2015). In the investigated samples, anzaite occurs in two distinct associations: (1) In most cases 10–30 μm sized anzaite replaces ilmenite (Figs. 5a–5d) and often shows patchy zonation, reflecting variable REE/Ti ratios (Fig. 5a). (2) Mostly in medium to highly serpentinized samples (restricted to TCB), however, 5–30 μm sized irregular grains or schlieren of anzaite occur, which are commonly associated and mostly intergrown with valleriite, but not with ilmenite (Figs. 5e and 5f).

DISCUSSION

The identification of fergusonite, REE-Ti-betafitte, cordylite, and britholite during this study represents the first described

occurrence of these REE minerals in the PCC and the first occurrence in a carbonatite complex of South Africa. Bulakh et al. (1998) mentioned a Ti-REE mineral and Karchevsky (2000) described a REE-silicate for the PCC, but both gave no further specifications on these minerals. The probable identification of anzaite represents its second occurrence worldwide.

Multistage formation of REE minerals in the Palabora carbonatites and phoscorites

Most REE mineralizations in carbonatites are believed to have crystallized from carbo- or hydrothermal fluids (e.g., Mariano 1989; Wall and Mariano 1996; Wyllie et al. 1996; Wall et al. 2001; Zaitsev et al. 2002; Williams-Jones et al. 2012; Nadeau et al. 2015). However, fluid inclusion studies show that REE do not preferentially fractionate into fluids, although they would be capable of transporting REE (Bühn and Rankin 1999). Experimental studies at high temperatures (Song et al. 2016) imply that carbonatite-related REE deposits may form by fractional crystallization of carbonatitic melts rather than from

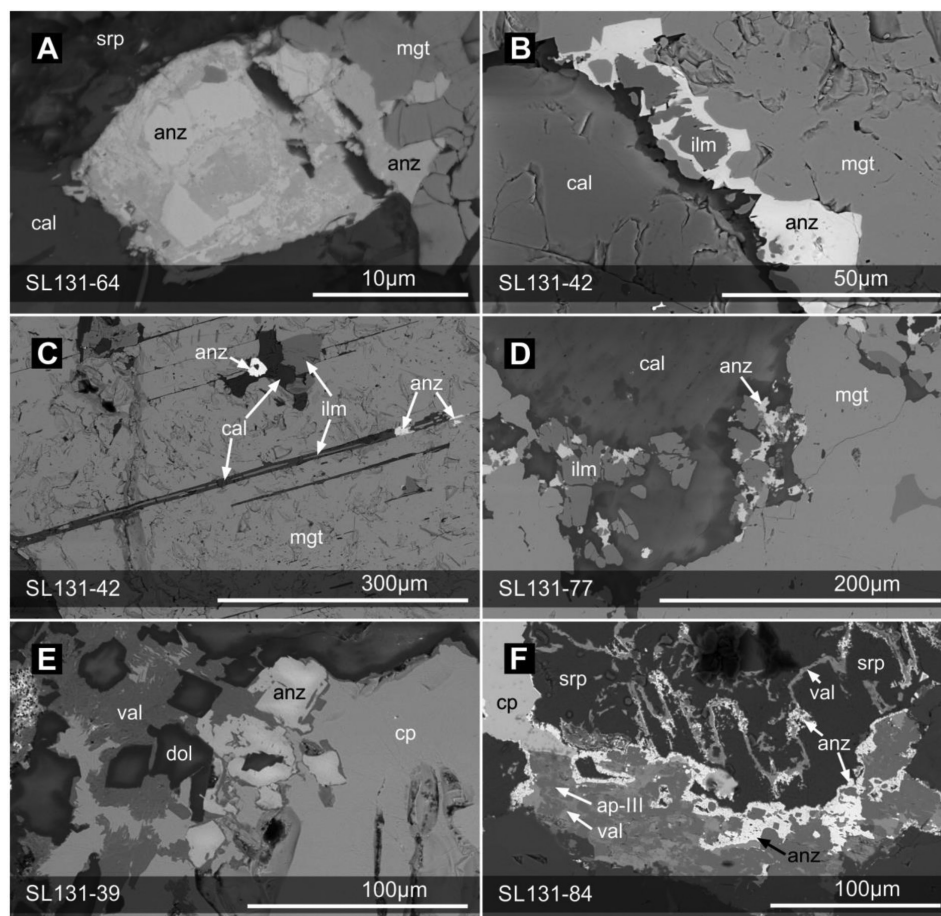


FIGURE 5. Textural appearances of anzaite. (a) Compositionally zoned anzaite completely replacing ilmenite in contact with magnetite. Anzaite shows mostly patchy zonation with the brightest areas having high REE/Ti ratios and the darker areas showing the opposite. (b) Anzaite replacing ilmenite with ilmenite relics enclosed by anzaite. (c) Dissolved ilmenite lamellae (partly filled with calcite) with relict ilmenite in the center of the lamellae and precipitation of anzaite within the former lamellae. The upper part of the image displays the same phenomenon with a batch of ilmenite partly dissolved and filled by calcite and showing marginal precipitation of anzaite. (d) Part replacement of ilmenite by anzaite as well as precipitation of anzaite around ilmenite relicts. (e) Anzaite associated with valleriite replacing chalcopyrite. (f) Association of anzaite, valleriite, serpentine, and secondary apatite (ap-III). Note the intergrowth of valleriite, ap-III, and anzaite.

exsolved hydrothermal fluids. In rare cases only, a magmatic origin for REE mineralizations in carbonatites is assumed, based on textural (e.g., Mountain Pass, Mariano 1989) and isotopic data (e.g., Zaitsev et al. 2002) with alteration, replacement, and remobilization of preexisting REE minerals clearly linked to a

late-stage process involving water-bearing fluids (e.g., Wall and Mariano 1996; Zaitsev et al. 1998, 2002; Wall et al. 2001; Moore et al. 2015). Some paragenetic studies on individual carbonatite complexes indicate multistage mineralization processes with significant overprint of the orthomagmatic mineralization by a

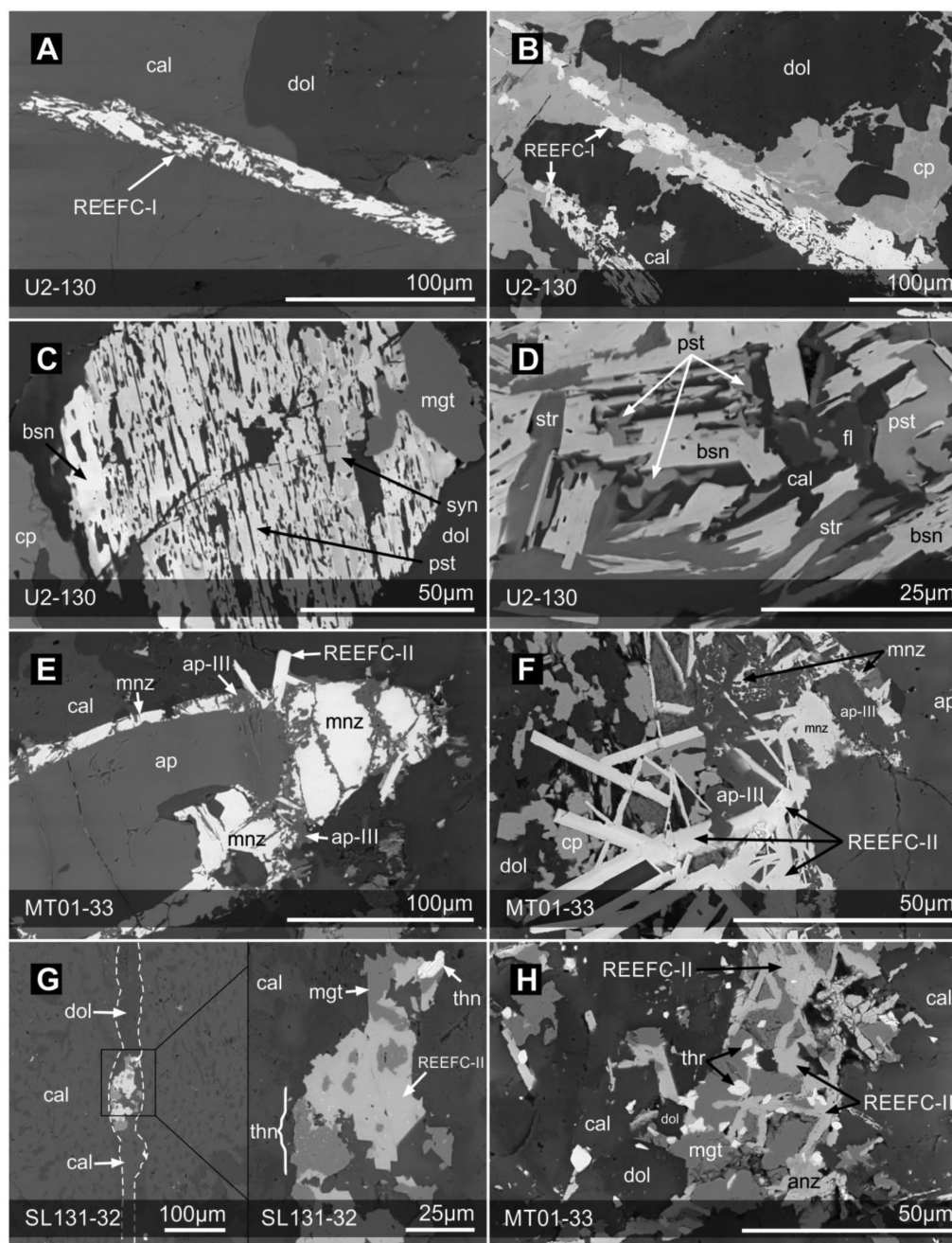


FIGURE 6. Textural appearances of REE-F-carbonates. (a) Partly dissolved REEFC-I needle. (b) REEFC-I partly included in chalcopyrite. Note the strong dissolved parts of REEFC-I outside the sulfide enclosure. (c and d) Partly dissolved REEFC-I with interdigitated parisite/synchysite and bastnaesite, and (d) the additional presence of strontianite and fluorite. (e and f) Relics of monazite around apatite with interlocked REEFC-II a. Monazite decomposed to secondary REEFC-II a needles and secondary apatite (ap-II). (g) Carbonate vein (marked with white dashed line) through calcite with exsolved dolomite and REEFC-II b. The enlargement shows the intergrowth with magnetite. Note the tiny secondary thorianite inclusions in magnetite and REEFC-II b. (h) REEFC-II b intergrown with magnetite and anazite with inclusions of secondary “fusiform” thorite. Recrystallized zone is located next to a serpentinized area.

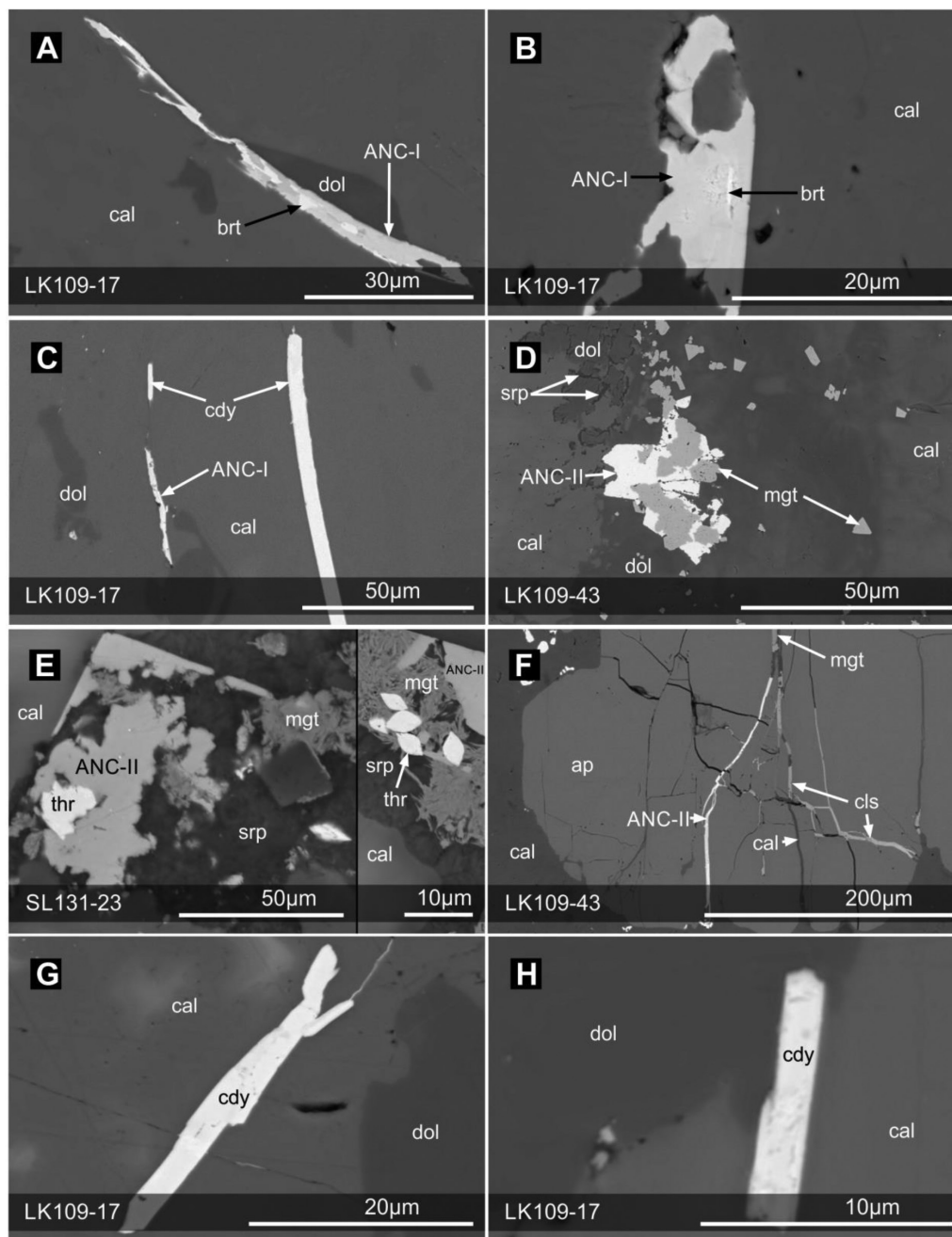


FIGURE 7. Textural appearances of ancylite and cordylite. (a) Heterogeneous ancylite needle with light parts reflecting intergrown baryte. The darkest parts reflect a high Ca, low Sr, and low REE contents and the medium light parts reflect a high Sr and low Ca content with a high concentration of REE. (b) Rod-like/partly irregular ancylite with an inclusion of baryte. (c) Ancylite associated with cordylite. (d) Ancylite intergrowth with magnetite in recrystallized carbonate vein. Dark rims around dolomite represent serpentine. (e) Ancylite pseudomorphed after completely dissolved primary thorianite, with a thorite inclusion enclosed in ancylite, serpentine, and magnetite, all associated with recrystallized calcite. (f) Cracks in apatite filled with ancylite, celestine, and magnetite. (g) Cordylite with a thin tail filling a crack in calcite. (h) Patchy zonation of cordylite shows the heterogeneity of this phase.

late-stage hydrothermal or carbothermal mineralization (Rankin 2005). Nevertheless, the controls on the REE mineralization in carbonatites are poorly understood (Trofantenko et al. 2016).

Based on the textures described above, the various REE

mineral associations at Palabora formed during different stages (Figs. 2 and 9). While fergusonite, REE-Ti-betafite, and probably also REEFC-I crystallized during the orthomagmatic stage directly from a carbonatitic melt, monazite and britholite

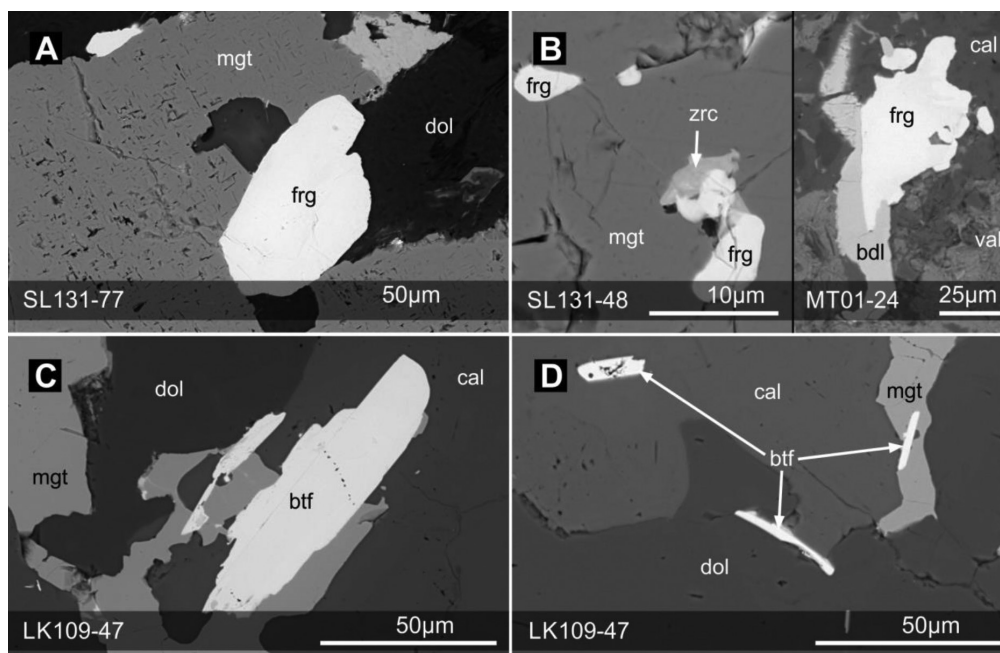


FIGURE 8. Textural appearances of fergusonite and REE-Ti-betafite. (a) Rounded fergusonite partly included in magnetite. (b) Rounded fergusonite associated with zirconolite included in magnetite and partly dissolved fergusonite with overgrown baddeleyite. Small baddeleyite grain on the left side in contrast shows an overgrowth by fergusonite. (c) Rod-shaped REE-Ti-betafite partly included in magnetite. (d) Rod-shaped REE-Ti-betafites included in magnetite, calcite, and dolomite.

precipitated from late-magmatic fluids (LM fluid). Finally, the formation of anzaite, REEFC-II (a+b) and ANC-II and the alteration of monazite and REEFC-I is assigned to REE redistribution processes caused by post-magmatic fluids (PM fluid). Although the genetic position of ANC-I and cordylite is not entirely clear, the association with baryte, the integrity of ANC-I, and the presence of cordylite needles next to strongly dissolved REEFC-I needles favor a formation during stage 4 (Fig. 2).

The variability of types of REE mineralization in the PCC largely reflects the sensitive character of REE mineral formation during fluid-assisted processes. We suggest that late-magmatic and post-magmatic fluids show compositional variabilities, which are probably caused by local dissolution-precipitation processes. We distinguish the following fluid types: LM = late-magmatic fluid enriched in REE, LM' = REE-depleted analog of LM that results from REE mineral precipitation from LM, PM = post-magmatic REE-poor or -free initial fluids, PM' = fluids enriched in REE by remobilization, PM'' = REE- and cation-enriched fluids transporting the element content for distal precipitation, and PM''' = REE-depleted fluids after REE mineral precipitation from PM' and PM''.

Orthomagmatic crystallization of fergusonite, REE-Ti-betafite, and REE-F carbonates

Texturally, fergusonite and REE-Ti-betafite are interpreted as early magmatic REE phases, which probably crystallized more or less contemporaneously. Fergusonite represents the most important Nb-phase in the system (pyrochlore *sensu stricto* is lacking), but its very low abundance reflects a general depletion of Nb in the Palabora carbonatites. Hence, the PCC comprises

a magmatic association of a Ti-poor Nb-oxide (fergusonite; <0.13 wt% TiO₂) and a Nb-poor Ti-oxide (REE-Ti-betafite; <0.11 wt% Nb₂O₅). Notably, Ti-bearing fergusonite (>1 wt% TiO₂) and Nb-bearing betafite (up to 20 wt% Nb₂O₅) have been described (e.g., Mitchell and Chakhmouradian 1998; Tomašić et al. 2006; Yaroshevskii and Bagdasarov 2008). At this stage it remains unclear why magmatic fergusonite and betafite in the PCC do not incorporate significant amounts of Ti and Nb, respectively. The enclosure of both mineral phases in magnetite isolates these minerals mostly from later fluid interactions and alteration (Fig. 9).

In general, REE-fluorocarbonates are among the most abundant REE minerals in carbonatites (Shunhua et al. 1986; Hsu 1992; Williams-Jones and Wood 1992). Although REE-F-carbonates (especially bastnäsite) are stable to temperatures above 600 °C (Wyllie et al. 1996 and references therein), most REE-fluorocarbonates precipitate at comparatively low temperatures (Williams-Jones and Wood 1992). Magmatic REE-F-carbonates (mainly represented by bastnäsite) from Mountain Pass were described as coarse-grained, hexagonal prismatic (strongly elongated), crystals in fine- to medium-grained calcite and baryte, while fine-grained, stubby, hexagonal, interstitial prisms of bastnäsite were formed by a late residual fluid (Castor 2008).

At Palabora REE-F-carbonates (REEFC-I) occur as small and elongated crystals that are partly dissolved and form optically continuous single crystals (Fig. 6a and 6b) and well-preserved REEFC-I needles are included in sulfides. Based on this and the similarities to REE-F-carbonates at Mountain Pass (except for crystal size), we assume a magmatic origin for

REEFC-I at Palabora.

Normally REE-F-carbonates contain minor amounts of Th (e.g., Armbrustmacher 1979; Smith et al. 2000; Humphries 2012). For example, bastnäsite typically contains 0.2–0.3 wt% Th (Wang et al. 2013) and can also occur as thorbastnäsite (Smith et al. 2000) with 47 wt% Th (Pavlenko et al. 1965). Uher et al. (2015) even report ThO₂ concentrations of 0.5 to 1.4 wt% for bastnäsite and 0.4 to 4.5 wt% for synchysite in a granite from Stupné, Slovakia. In our case, REEFC-I are Th-poor (<0.08 wt%), which is in contrast to REEFC-II (see below). We suggest that early magmatic precipitation of Th-minerals (mostly thorianite; Figs. 2 and 3b) caused an early depletion of Th in the magmatic system, which resulted in lower Th concentrations during the stage of REEFC-I precipitation. Furthermore, partly dissolved REEFC-I (Fig. 6a) indicates a later remobilization of REE and the patchy appearance of parisite and synchysite within the bastnäsite interdigitation indicates an alteration of bastnäsite to synchysite and parisite during the remobilization of REE (see below).

Late-magmatic formation of monazite and britholite at the expense of apatite and forsterite

Monazite formation. The replacement of apatite by monazite has been described for some hydrothermal deposits (e.g., Pan et al. 1993a; Liefink et al. 1994; Smith et al. 1999) as a late-stage alteration phenomenon (Wall and Mariano 1996). Monazite inclusions and rims around apatite are often explained by fluid-induced (metasomatic) alteration of apatite via coupled substitution and mass transfer (Harlov et al. 2002, 2005; Harlov and Förster 2003). As such, monazite may have originated from the REE budget available

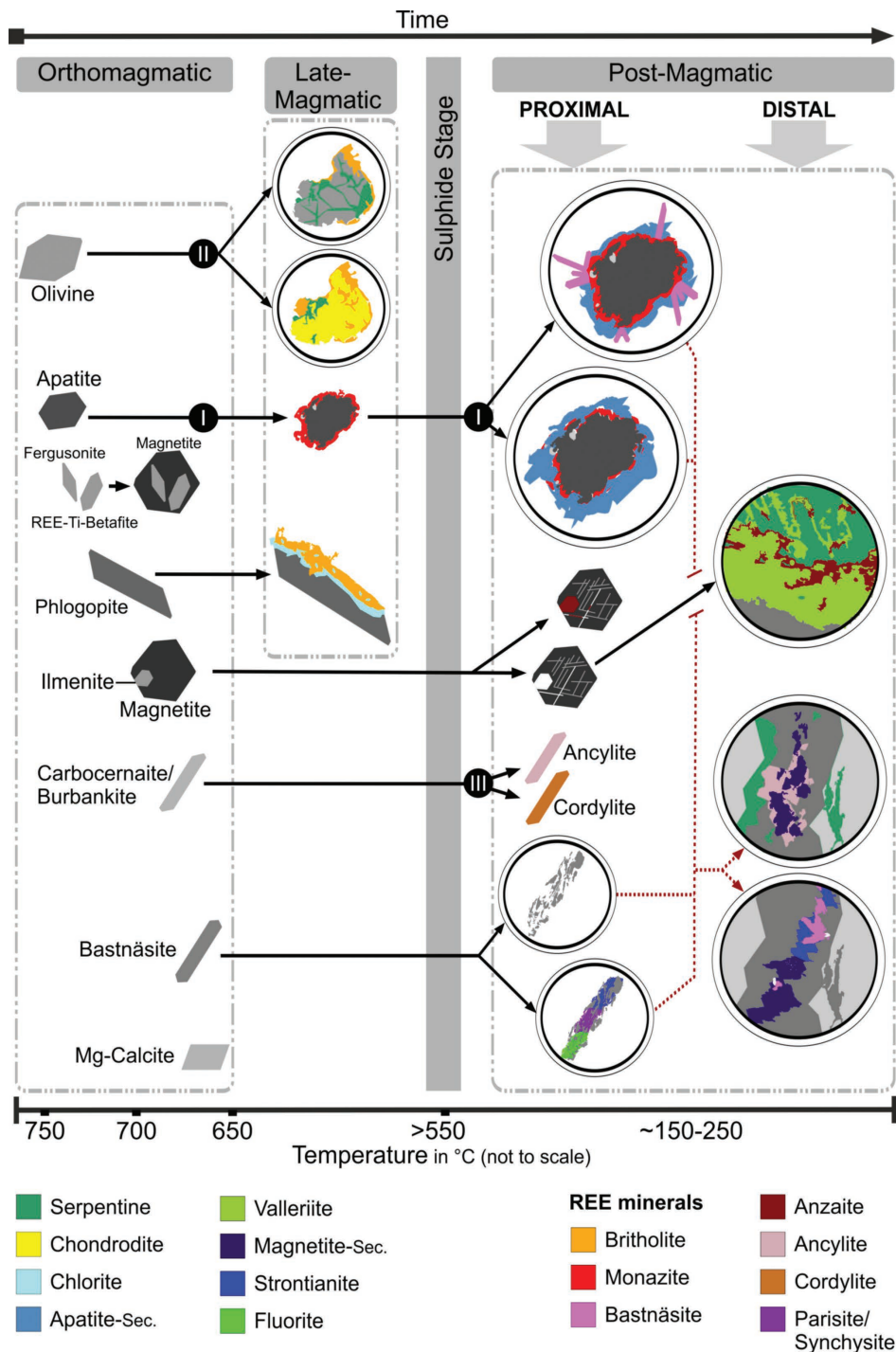


FIGURE 9. Scheme for REE mineral precipitation during different evolutionary stages of the Palabora carbonatites. Estimated temperatures after (Fernandez et al. 1977; Solovova et al. 1998; Fleet 2006; Sharygin et al. 2011; Chakhmouradian et al. 2015). Roman numerals (I–III) refer to diagrams in Figure 10.

from the apatite itself, where Si and Na would be removed from the apatite without the concurrent removal of REE (Pan et al. 1993a; Harlov and Förster 2002; Harlov et al. 2002).

In the investigated samples there is no textural evidence to

suggest that monazite is the result of exsolution from precursor apatite during metasomatic alteration. Rather, apatite shows strong dissolution textures. Mass-balance considerations imply that the REE content of the apatite is not sufficient to allow for the precipitation of the observed amounts of monazite (Figs. 4a and 4b). We suggest that the precipitation of monazite (in cases associated with calcite) at the expense of apatite was caused by a REE-bearing fluid, according to the following schematic equation:

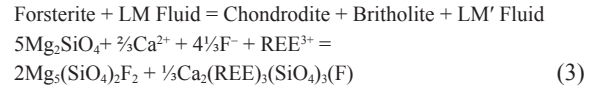
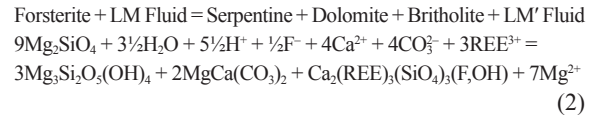


Due to the relative immobility of P (Smith et al. 1999; Poi-trasson et al. 2004; Cetiner et al. 2005; Louvel et al. 2015), monazite mainly precipitates directly at the contact to apatite or within

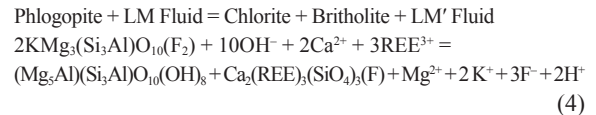
its immediate vicinity. The different appearances from surficial dissolution (thin rims of monazite around euhedral apatite; Fig. 4a) to nearly complete dissolution (larger masses of monazite with relict apatite; Fig. 4b) probably reflect variable degrees of apatite replacement by monazite linked to the degree of apatite dissolution by the fluid.

Britholite formation. Britholite is mainly described from nepheline syenites and contact metasomatic deposits, where it generally forms during hydrothermal processes related to the replacement of apatite or monazite (Budzyń et al. 2011; Uher et al. 2015; Zirner et al. 2015). Britholite has also been described as a low-temperature phase in the Virulando carbonatite (Angola) where it formed during late-stage supergene alteration processes, associated with synchysite, cerite, goethite, hollandite, and baryte (Torró et al. 2012). In all, britholite is assumed to have a late stage to post-magmatic (subsolidus alteration of primary minerals) origin for most occurrences (Wall et al. 1993; Uher et al. 2015).

Typically, britholite obtains the necessary anions from Si-bearing hydrothermal fluids. However, because of a general lack of Si-rich fluids in carbonatitic systems, another Si source has to be considered. Based on textural evidence, we suggest that Si is provided by the serpentinization of forsterite and the replacement of forsterite by chondrodite to which britholite is largely bound (Fig. 4f, 4g, and 9). As forsterite is REE-poor, the britholite-forming fluid contained appreciable amounts of REE, in accordance with the assumptions made for monazite formation above:



In a few cases britholite formation is associated with the chloritization of phlogopite:



Although britholite from Palabora is generally F-rich (fluor-britholite; Fig. 10 II), britholite associated with the replacement of forsterite by chondrodite and the chloritization of phlogopite is higher in F than the britholite associated with the serpentinization of forsterite. This shows that the LM fluid contains variable contents of F (Fig. 10 II).

Based on textural observations (Fig. 4e), we suggest that monazite and britholite formed contemporaneously from the same fluid (Fig. 9). Accordingly, the type of REE phase formed depends on the local presence of forsterite or apatite, which provide the necessary SiO_4^{4-} or PO_4^{3-} , respectively. The occasional presence of acicular ap-II in serpentine indicates that small amounts of P (released by monazite formation; confirmed by mass-balance calculations or dissolution of apatite) may cause precipitation of secondary apatite during serpentinization of forsterite. The absence of REE

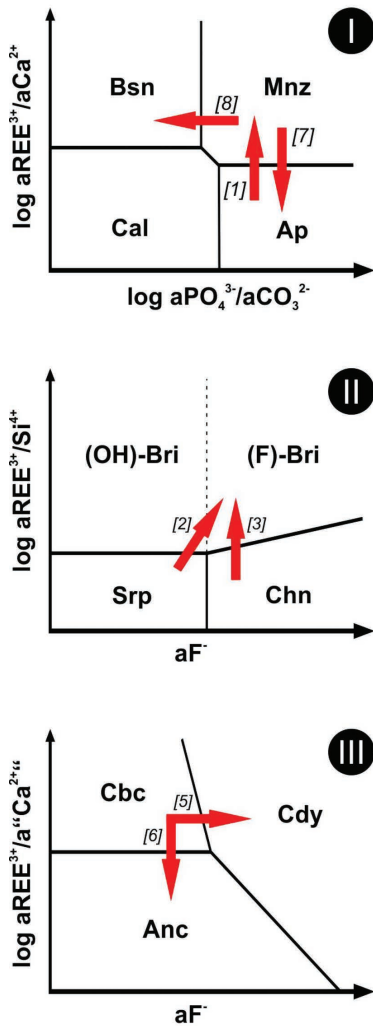


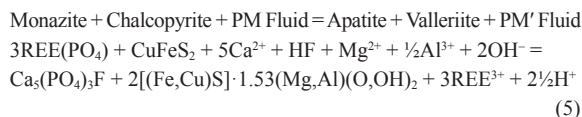
FIGURE 10. Qualitative activity diagrams illustrating the relative stabilities of different REE mineral phases. Numbers in parentheses refer to reactions mentioned in the text. Note the necessity of REE introduction for the formation of monazite and britholite during stage 2 (I and II) as well as the locally controlled variability of F in stage 2 and 4 fluids (II and III). The activity of “Ca²⁺” in diagram III reflects the combination of the alkali- and alkaline earth metals Na⁺+Ca²⁺+Sr²⁺+Ba²⁺ for simplification.

in olivine and the too low concentrations in apatite indicates the necessity to import REE into the system to precipitate britholite and monazite (arrows labeled 1–3 in Fig. 10).

Post-magmatic redistribution of REE: Formation of cordylite, ancylite, REE-F carbonates, and anzaite

Cordylite and ancylite (ANC-I) formation. Whereas ancylite is a relatively common REE mineral in carbonatites, cordylite is extremely rare (Zaitsev et al. 1998). Ancylite has never been described as a primary magmatic mineral, instead it is specified as a useful indicator of hydrothermal/carbothermal processes (Wall and Zaitsev 2004a; Verplanck et al. 2016). Zaitsev et al. (1998) describe the association of cordylite and ancylite as resulting from the hydrothermal alteration of magmatic carbocernaite and burbankite. Based on this and our own textural observations (see above), we suggest that cordylite (Fig. 7g) and ANC-I (Figs. 7a–7c), together with baryte and strontianite with which it is tightly associated, may replace precursor REE-Ca-Sr-carbonates. Because of the absence of any relics it is not possible to identify the precursor mineral of cordylite and ANC-I. However, based on very similar textural descriptions in the literature (Pecora and Kerr 1953; Somina 1975; Kapustin 1980; Zaitsev et al. 1998; Moore et al. 2015), we assume the former presence of carbocernaite/burbankite (red question mark in Fig. 2). Burbankite and/or carbocernaite are important REE minerals in carbonatites that were probably present in many carbonatites but are typically replaced by ancylite, strontianite, synchysite, calcite, baryte, quartz, monazite, and apatite (e.g., Kangankunde, Malawi; Wigu Hill, Tanzania; Adiounedj, Mali; Bear Lodge, Wyoming, and Gem Park, U.S.A.; Wall et al. 1997). Supposing the precipitation of cordylite and ancylite during the early phase of stage 4 (Fig. 2 and 9), we suggest that dissolution of REEFC-II (see below) controls the activity of F in the fluid, which in turn controls the formation of ancylite and cordylite (Fig. 10 III). Ancylite and cordylite are depleted in Th, which suggest that the fluid from which they precipitated from was also Th-poor. The later precipitation of secondary thorianite and thorite, as well as slightly higher Th contents in later secondary REE minerals, suggest Th-enrichment of the fluid by dissolution of primary Th minerals.

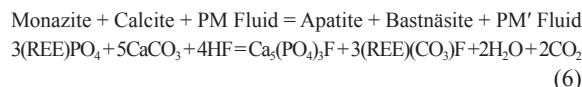
Monazite alteration. Monazite in contact with or enclosed by sulfides is occasionally altered to ap-III associated with the valleriitization of the sulfide (Figs. 4c, 4d, and 9). This may be caused by the remobilization of REE from monazite (Fig. 10 I) by the same fluid that caused valleriitization of sulfides and can be explained by the following schematic equation:



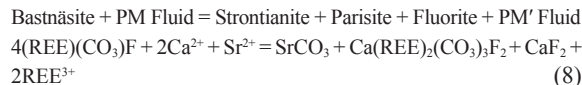
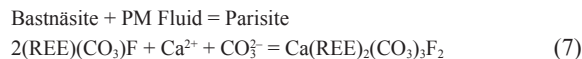
Valleriitization in association with ap-III formation sometimes includes thorite (Fig. 4d), which is supposed to be formed by the remobilization of Th from primary Th minerals by a post-magmatic fluid.

REEFC-II formation. REEFC-II show two different types of occurrence, which may be distinguished into a proximally

(REEFC-II a) and a distally precipitated (REEFC-II b) variety depending on the REE saturation of the fluid (Fig. 9). The proximal variety (Figs. 6e and 6f) indicates reaction of monazite, apatite, and a fluid, which is linked to reaction 5 with the exception of the availability of CO_3^{2-} by the dissolution of carbonate. The remobilization of REE during this reaction will be prevented by the formation of REEFC-II a (exclusively bastnäsite), similar to what was observed in the Bayan Obo deposit (Smith et al. 1999):

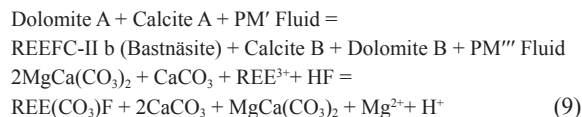


Partial dissolution of REEFC-I (see above) may form strontianite, parisite/synchysite and fluorite in the interstices of the REEFC-I interdigitation (Figs. 6d and 9). This may cause additional remobilization of REE by the evacuation of dissolved components $[(\text{REE})(\text{CO}_3)\text{F} \leftrightarrow \text{REE}^{3+} + \text{CO}_3^{2-} + \text{F}^-]$. The alteration of REEFC-I to parisite and synchysite may be caused by interaction with a Ca-rich fluid, while the presence of Sr promotes additional precipitation of strontianite and fluorite:



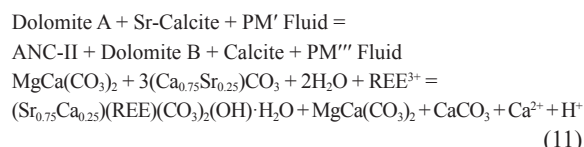
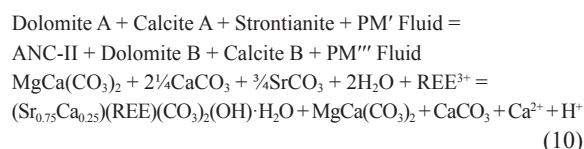
The observation that REEFC-I needles, protected as inclusions in sulfide (Fig. 6b), do not show the described alteration, indicates that this process happens after the formation of sulfide minerals and during the post-magmatic stage.

The second variety (distal; REEFC-II b) precipitated in vein-like fluid paths together with secondary strontianite, magnetite, anzaite, valleriite, thorianite, and thorite (Figs. 6g, 6h, and 9). Thus, the fluid causing the precipitation of these secondary minerals was probably enriched in Th. Thorium can be remobilized by leaching and dissolution of primary Th-bearing minerals such as thorianite (Pan et al. 1993b). At high temperatures, Th can be incorporated into REE minerals (Harlov et al. 2011), whereas at low temperatures, Th incorporation into REE minerals is restricted (Read et al. 2002; Doroshkevich et al. 2008; Budzyń et al. 2010), which explains the coexistence of secondary Th minerals with REEFC-II b (Figs. 6g and 6h). In fact, Th contents in REEFC-II are higher than in REEFC-I, but the depletion of Th in REEFC-I depends on the depletion of Th in the melt during REEFC-I precipitation after the early crystallization of Th minerals (see above). At the same time, REEFC-II b formed concurrently with Th minerals due to the remobilization of Th from primary Th minerals. Formation of REEFC-II b may have occurred according to the following schematic reactions:



The percolating fluid that caused the formation of REEFC-II b further induced dissolution (calcite A and dolomite A) and recrystallization (calcite B and dolomite B) of carbonates constituting a further generation of carbonates within veins (Fig. 6g).

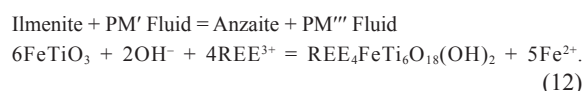
Ancylite (ANC-II) formation. Similarly, ANC-II is bound to vein-like fluid paths with a secondary mineralization of carbonates (Fig. 7d). However, ANC-II was not observed to coexist with REEFC-II b. Rather, in cases where REEFC-II b are present, the dominant Sr phase is a REE-poor strontianite ($\Sigma \text{REE}_2\text{O}_3 < 4 \text{ wt\%}$; Karchevsky 2000) and the REE are mainly incorporated into REEFC-II b (Fig. 9). At presumably higher H_2O activities, the formation of serpentine and the absence of the REEFC-II b lead to the concentration of REE into the Sr phase ancylite. The necessary Sr was probably provided by the dissolution of strontianite and/or Sr-rich calcite (which occurs as secondary exsolutions in exsolved dolomite):



Anzaite formation. Anzaite-(Ce) was first described from Afrikanda (Russia) as a late hydrothermal alteration product where Ti and Fe were derived from primary Ti oxides such as ilmenite. This is reflected by a ubiquitous association of anzaite with ilmenite and/or Ti-rich magnetite (Chakhmouradian et al. 2015). The associated mineral assemblage precipitated at Afrikanda at 150–250 °C, $\text{aH}^+ \approx 10^{-5}$ and $\text{aH}_4\text{SiO}_4^0 > 10^{-4}$ (Chakhmouradian and Zaitsev 2004).

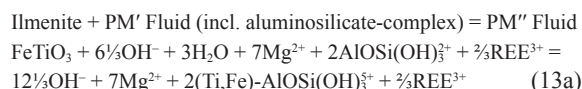
The close association of anzaite with valleriite (Figs. 5e and 5f) at Palabora confirms the assumption of a low-temperature origin. Anzaite is texturally bound to ilmenite (Figs. 5b and 5d). Therefore, the partial dissolution of ilmenite by a REE-bearing fluid seems to be essential for the local enrichment of Ti allowing for the formation of anzaite. Two different occurrences of anzaite can be distinguished, which might reflect a proximal and distal fluid transport (Fig. 9) of a Ti-enriched, REE-bearing fluid.

The common association includes anzaite with relics of ilmenite in direct contact or close vicinity with magnetite (Figs. 5a–5d). In this case, anzaite directly replaces ilmenite, which can be described by the following schematic equation:

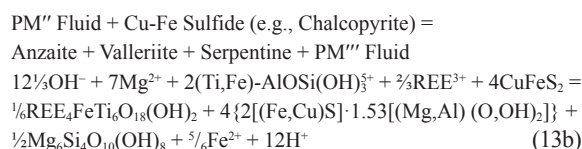


The less common occurrence of anzaite is not directly bound to ilmenite but associated with valleriite and serpentine (Figs. 5e and 5f). This association requires small-scale hydrothermal transport of Ti, Al, and Si by a REE-bearing fluid. In general,

very low pH fluids, combined with the availability of complexing ligands such as F, can enable Ti transport (van Baalen 1993). However, we consider such low pH values (<2) unlikely for Palabora. Alternatively, significant mass transfer of Ti has been explained by complexing agents of polymerized silicate molecules in solution (Manning 2004), most likely Ti-aluminosilicate complexes (Tropper and Manning 2005; Beitter et al. 2008). We favor this explanation as the assumption of the existence of Ti-transporting aluminosilicate complexes provides Al and Si for valleriite and serpentine formation, respectively (as observed; reaction 13b). The precipitation of this type of anzaite together with valleriite may be expressed by a two-step process. First, ilmenite is dissolved and Ti-aluminosilicate-complexes form:



This Ti-enriched fluid may then precipitate anzaite together with valleriite and serpentine when coming into contact with sulfides:



The type of anzaite formation (proximal or distal; Fig. 9) depends on the availability of potential Ti-complexing ligands and is therefore locally controlled by the earlier enrichment of Si and Al.

Although Kavecsanszki et al. (2012) assume that the sulfide-bearing liquid (stage 3) released fenitizing fluids, the actual source of the PM fluid has not yet been demonstrated. Alternatively, external fluids, e.g., related to the cross-cutting dolerite dikes, may have caused post-magmatic alteration reactions within the carbonatites.

IMPLICATIONS

Our new data reveal a complex interplay between host minerals, fluid chemistry, and REE mineralogy after the orthomagmatic stage. This interplay leads to various local chemical (micro) environments reflected in different REE mineral assemblages. Our results suggest that hydrothermal processes during late-magmatic and post-magmatic stages are of greater importance with respect to the formation and variability of REE minerals than orthomagmatic crystallization. Hydrothermal overprint causes alteration and in some cases complete replacement of primary REE minerals. Our study on the Palabora carbonatites further implies that the REE contents of magmatic minerals (such as apatite and carbonates) are not high enough to account for the formation of late-magmatic REE minerals such as monazite, which suggests that a REE-enriched fluid was introduced into the observed sections of the complex during late-magmatic stages. The results of this study confirm (1) the significance of late-stage introduction of REE and their reaction with precursor mineral phases, and (2) the redistribution of REE during post-magmatic stages in natural carbonatitic systems.

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In a special way, we remember Pavel I. Karchevsky (1976–2002) whose study about the rare earth mineralization of the PCC was a significant cornerstone for our work.

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