The petrogenesis of carbonatites:

Mineral variations and effects on the REE mineralization

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Dissertation

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DECLARATION

I, Robert Johannes Giebel, declare that the thesis (inclusive of published articles) that I herewith submit for the Doctoral Degree of Philosophy at the University of the Free State, is my independent work, and that I have not previously submitted it for a qualification at another institution of higher education.

R. Johannes Giebel

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ABSTRACT

Carbonatites have high economic potential and are important sources for a range of commodities, including P, Fe, F, Cu, high field strength elements (HFSE, e.g., Zr, Hf, Nb, U), and especially the rare-earth elements (REE). About 10% of all known carbonatite occurrences (50 out of 550) are currently mined for those commodities and about 40% of all REE exploration projects target carbonatites and associated rock types. Despite their economic importance we have a limited understanding of carbonatite systems and their relationship with associated rock types. A range of processes result in strong variability in the mineralogy and mineral chemistry of carbonatites, and hence their economic viability. However, scientific interest in understanding the complex mineralizations and associations in carbonatitic systems has tremendously increased. Our studies focused on two carbonatite complexes, namely the Palabora Carbonatite Complex (South Africa) and the Kaiserstuhl Volcanic Complex (Germany), that display a variety of mineral assemblages and mineral chemistries. The Palabora carbonatite clearly indicates an insignificant orthomagmatic REE mineralization, a late-magmatic enrichment of REE mineral phases and an effective post-magmatic redistribution of the REE mineralization. The Kaiserstuhl carbonatites, on the other hand, show a greater diversity in their REE concentrations due to a wider range of petrogenetic processes. Some of the Kaiserstuhl carbonatite bodies experienced a strong hydrothermal enrichment of REE. In contrast, one Kaiserstuhl carbonatite body, namely the Badberg, shows strong retention of REE by apatite during early orthomagmatic stages. This carbonatite body lacks a late-magmatic to hydrothermal REE enrichment. The enhanced incorporation of REE into orthomagmatic apatite is attributed to a coupled substitution that is promoted by host rock contamination. Since the REE-hosting mineral type, its abundance and its mineral associations are some geological influences on a carbonatite being economically viable or not, understanding the causes and modifications of REE mineralization is of crucial importance.

We use the Palabora complex (and the Fen complex, Norway) to illustrate the individual evolutionary stages of those carbonatites. At the Kaiserstuhl complex we illustrate the influence of external silicate contamination on the economic potential of a carbonatite. Furthermore, we present a new model that reconstructs the emplacement of, and relation between, carbonatites and associated rocks. This model predicts the ratio between carbonatites and associated rock types. It also explains the origin of phoscorite magmas.

Keywords: The Palabora Carbonatite Complex, The Kaiserstuhl Volcanic Complex, Rare-Earth-Elements, Carbonatites, Phoscorites, Mineral Variations, Mineralogy and Mineral Chemistry, Petrogenesis and Multi-Stage Evolution, Hydrothermal and Magmatic Processes, Emplacement Model.

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DESCRIPTION OF PERSONAL CONTRIBUTION

Each authors' contributions to publications within this thesis are declared in the following tables.

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Giebel, RJ	**1**	**75**	**90**	**83**	**66**
Gauert, CDK	2	5	0	2	5
Marks, MAW	3	10	0	10	22
Costin, G	4	0	10	0	2
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Giebel, RJ	**1**	**77**	**100**	**81**	**68**
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Gauert, CDK	3	3	0	4	5
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Walter, BF	3	21	30	15	7
Braunger, S	4	22	0	24	12
Marks, MAW	5	23	0	20	32
Wenzel, T	6	0	20	0	0
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Dietzel, CAF	1	15	45	35	35
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Dahlgren, S	3	30	5	10	5
Giebel, RJ	**4**	**0**	**5**	**10**	**5**
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Appendix

1. INTRODUCTION

1.1 Genesis of carbonatites and associated rocks

Carbonatites are mantle-derived igneous rocks that contain ≥50 vol.% carbonate minerals (Le Maitre et al., 2002). About 550 occurrences are known worldwide. Most of them (80%) are associated with typically SiO_2 undersaturated silicate rocks (Mitchell, 2005; Woolley and Kjarsgaard, 2008) that span a wide compositional range. Carbonatites can be subdivided into calcio- (formerly named sövites if coarse grained and alvikites if fine grained calcite carbonatites), magnesio- (former beforsites) and ferro-carbonatites, depending on their predominant carbonate phase. Calcio-carbonatites are the most common carbonatite type (Woolley and Kempe, 1989). Less common are primary magmatic dolomitic and ankeritic carbonatites. Petrogenetic models for the origins of carbonatites have been reviewed by e.g. Bell (1989), Lee and Wyllie (1994, 1997), Mitchell (2005), and Jones et al. (2013). Two formation processes are accepted:

(1) Derivation from a primary carbonatitic magma by low-degree partial melting of carbonate-bearing mantle (Bell and Simonetti, 2010; Dalton and Presnall, 1998). The primary melt composition is, however, still unclear and under debate.

(2) Derivation from a carbonate-bearing silicate magma by either: (2a) fractional crystallization (Lee and Wyllie, 1994), or (2b) separation of a carbonatitic magma from a carbonate-bearing silicate magma by liquid-liquid immiscibility (Veksler et al., 1998).

Some carbonatites (~4%) are spatially, temporally and genetically associated with phoscorite rocks, which are defined as carbonate-bearing ultramafic rocks comprised mainly of magnetite, apatite and forsterite/diopside/phlogopite. Phoscorites almost exclusively occur in multiphase carbonatite complexes and are situated in or around carbonatite cores (Krasnova et al., 2004b). Small-scale phoscoritic structures are present in many carbonatites (Krasnova et al., 2004b), but mostly poorly described.

The genetic relationship between carbonatites and phoscorites has been discussed among petrologists for many years. Two potential processes have been suggested for the generation of phoscorites:

(1) Derivation from an individual phoscoritic magma. However, the formation from an individual magma is specified as unrealistic because of the instability of phoscoritic melts at plausible temperatures (Lindsley and Epler, 2017).

(2) Derivation from a carbonatitic magma by either: (2a) fractional crystallization, or (2b) separation from a parental carbonatitic melt by liquid-liquid immiscibility (Krasnova et al., 2004b). Both processes may explain the common geometric relations between carbonatites and phoscorites (Krasnova et al., 2004b). Spherulitic and orbicular textures of phoscorite portions within carbonatites and vice versa in numerous carbonatite complexes (e.g., Krasnova et al., 2004b; Lapin and Vartiainen, 1983), as well as mineral inclusions in apatite and olivine (Mikhailova et al., 2002), are evidence for phoscorite formation by liquid immiscibility. In addition, melt inclusions show Fe and P enrichment in parental magmas of some carbonatites (e.g., Chen et al., 2013; Guzmics et al., 2008; Krasnova et al., 2004b). Phoscorites, however, contain carbonate-dominated melt inclusions (e.g., Veksler et al., 1998; Zaitsev and Kamenetsky, 2013). Even though liquid immiscibility plays an important role in phoscorite genesis, the role of fractional crystallization is still under debate for some magmatic complexes (e.g., Rimskaya-Korsakova and Krasnova, 2002). The formation of many carbonatite occurrences and their relationships to associated rocks remains unclear, but detailed mineralogical and mineral chemical investigations may reveal relevant formation processes (see above).

1.2 Mineralogical and mineral chemical variations in carbonatites/phoscorites

The most common non-carbonate minerals in carbonatites and phoscorites are apatite, magnetite and phlogopite. Apatite and phlogopite in particular have wide ranges in composition (e.g., Brod et al., 2001; Chakhmouradian et al., 2017; Chakrabarty et al., 2009; Hogarth, 1989; Mitchell et al., 2017). Therefore, they are useful monitors for the magmatic and hydrothermal evolution of carbonatitic systems (e.g., Brigatti et al., 1996; Chakhmouradian et al., 2017). Apatites from carbonatites and phoscorites may accommodate higher concentrations of Sr, REE as well as Na and Si compared to apatites from most other magmatic rocks. The halogen-site is primarily occupied by OH and F, whereas Cl concentration is typically very low (e.g., Teiber et al., 2015). Micas in carbonatites (and phoscorites) can be separated into four main groups: (1) Phlogopite-annite, (2) phlogopite-eastonite, (3) phlogopite-kinoshitalite, and (4) phlogopite-tetraferriphlogopite series (e.g., Reguir et al., 2009 and references therein). These micas are very Mg-rich (phlogopite) and typically evolve towards an Al-rich composition (eastonite and kinoshitalite; e.g., Brod et al., 2001; Lee et al., 2003) or an $^{IV}Fe^{3+}$-rich composition (tetraferriphlogopite;

e.g., Brod et al., 2001; Gaspar and Wyllie, 1987). In contrast, micas in associated silicate rocks typically contain a significant annite ($^{VI}Fe^{2+}$) component (>20%) and are thus classified as biotites.

A number of other silicate minerals (e.g. monticellite, forsterite, clinopyroxene, foid, alkali feldspar, etc.) have been described (Barker, 2001) in carbonatites, but it is difficult to distinguish primary carbonatitic mineral phases from xenocrysts (Barker, 2001). In this context, a mineral chemical comparison of silicate minerals in carbonatites and cogenetic silicate rocks, country rocks and mantle rocks, can provide insights on their provenance. However, relevant studies are rare (e.g., Vuorinen and Skelton, 2004). Furthermore, various HFSE-rich minerals and sulphides (pyrrhotite, pyrite, chalcopyrite, etc.) are commonly present (e.g., Bell et al., 2015; Chakhmouradian, 2006; Farrell et al., 2010; Gomide et al., 2013). A detailed understanding of mineral variability and their process-related characteristics are crucial to understand how carbonatitic complexes are emplaced and how their mineralizations develop. This understanding is critical to mineral exploration and future development of these important resources (Moore et al., 2015).

1.3 REE mineralization in carbonatites and phoscorites

Carbonatites and phoscorites are lithologies of high economic interest and a some are currently mined for their HFSE mineral-bearing phases (e.g., Nb in pyrochlore; Zr in baddeleyite; REE in monazite and REE-fluorcarbonates, etc.; e.g., Niobec, Canada; Kovdor, Russia; Mount Weld, Australia; Bayan Obo, China; Gendron et al., 1984; Ivanyuk et al., 2002; Kanazawa and Kamitani, 2006; Krasnova et al., 2004a; Yang et al., 2011). Additionally, they can represent important sources for Fe (magnetite) and P (apatite; e.g., Palabora, South Africa; Kovdor, Russia; e.g., Hanekom et al., 1965; Ivanyuk et al., 2002) and other minor commodities. About 45 REE-minerals and REE-bearing minerals have been reported in carbonatites worldwide (Chakhmouradian and Zaitsev, 2012; Wall and Zaitsev, 2004; Zaitsev et al., 2015). Two general types of REE mineralization can be distinguished in carbonatites: (1) those with “true” REE-minerals where REE are major constituents and (2) those where independent REE-minerals are absent and the significant amounts of REE are hosted in minerals such as calcite and apatite (Wall and Zaitsev, 2004). A variety of those minerals may be found within a single carbonatite. The most common REE-minerals in carbonatites are ancylite, bastnäsite-group minerals (known as REE-fluorcarbonates), britholite, and monazite (Mariano, 1989; Zaitsev et al., 1998; Zaitsev et al., 2014), which are interpreted to be either of magmatic (relatively rare, mostly bastnäsite/parisite; Chakhmouradian and Zaitsev, 2012; Moore et al., 2015), hydrothermal (mostly bastnäsite and monazite; Williams-Jones et al., 2012) or supergene origin (e.g., crandallite-group minerals in carbonatite-derived laterites; Kynicky et al., 2012). Numerous carbonatite complexes experienced a multi-stage evolution (e.g., Brigatti et al., 1996; Lee et al., 2003; Moore et al., 2015), with processes potentially responsible for REE enrichment including 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). But in general, several studies pointed out that hydrothermal processes usually are the most important parameter to form a major REE mineralization (e.g., Barra do Itapirapua, Bear Lodge, Tundulu and Kangankunde, Khibina; Andrade et al., 1999; Moore et al., 2015; Wall and Mariano, 1996; Zaitsev, 1996).

1.4 Case studies of carbonatite deposits

Some of the best studied REE-rich carbonatite complexes are those of the Kola Province (Finland and Russia). Phoscorites and early-stage carbonatites of most of these complexes are relatively REE-poor (≥2000 µg/g). The REE is generally hosted in major rock-forming minerals such as calcite and apatite, whereas REE-minerals are mostly absent. Late-stage carbonatites, however, show high REE contents (up to 5 wt.%) and incorporating distinct REE-minerals (e.g., bastnäsite; Lee et al., 2004; Zaitsev et al., 2015). Additionally, primary (crystallized from a melt or carbo-hydrothermal fluid) and secondary (formed during metasomatic replacement) REE mineralizations are distinguished (Zaitsev et al., 2015).

A good example for the complexity of multi-stage REE mineralizations is the Bear Lodge carbonatite (USA), where five distinct REE-mineral assemblages can be texturally distinguished that record multiple stages of hydrothermal deposition involving compositionally distinct fluids followed by supergene oxidation (Moore et al., 2015). Similar processes were documented from several other carbonatite complexes in Russia, China, Finland, Malawi and Siberia (Al Ani and Sarapää, 2009; Bulakh et al., 1998; Chakhmouradian and Zaitsev, 2012; Wall and Mariano, 1996; Xu et al., 2010; Zaitsev et al., 2002; Zaitsev et al., 1998). In several of these cases, changes in temperature and in activities of CO_2, HF and HCl in such fluids (caused e.g., by the dissolution of primary minerals such as carbonates, apatite or phlogopite) are assumed to be responsible for the variability of observed REE mineralizations (Andersen and Austrheim, 1991; Downes et al., 2014).

The formation of the world's currently largest producing REE deposit Bayan Obo (China) was also explained by carbonatite-derived multistage hydrothermal metasomatism, in this case of sedimentary carbonate rocks (e.g., Chao, 1997). The Bayan Obo deposit contains several distinct REE mineralizations. The dominant REE-minerals are bastnäsite and monazite, which are assumed to have precipitated from CO_2-rich fluids (Kanazawa and Kamitani, 2006). The broad variation in fluid compositions (as indicated by fluid inclusion data) points to multistage deposition and remobilization of the REE.

In the world's second largest REE deposit, Mountain Pass (USA), three distinct REE-mineral assemblages include magmatic bastnäsite, parisite and monazite, late-stage bastnäsite and secondary synchysite, sahamalite and ancylite (Castor, 2008). Interestingly, textural observations in these rocks indicate an upward streaming of REE- and Ca-rich fluids. In this case, fluids of distinct compositions had the potential to precipitate REE-minerals and to modify pre-existing REE mineralizations.

In summary, REE deposits in carbonatites are diverse and often show a multi-stage origin. The REE mineralizations within a single orebody can be highly variable and precipitated from a range of temperatures, pressures, pH and fluid compositions (e.g., Cooper et al., 2015). REE mineralizations in carbonatites can be of primary magmatic origin, but many are attributed to changes in REE speciation and complexation during the transition from magmatic to hydrothermal/carbothermal stages (Haas et al., 1995).

This thesis focuses on the Palabora Carbonatite Complex (PCC) (South Africa) and the Kaiserstuhl Volcanic Complex (KVC) (Germany). The former is one of the deepest emplaced carbonatite occurrences worldwide and is associated with a prominent phoscorite occurrence. The latter reflects a shallow, subvolcanic emplacement including several geometrically distinct carbonatite bodies, and no associated phoscorite. The investigation of the Palabora and Kaiserstuhl complexes, which are described in more detail below, was a unique opportunity for a systematic study on mineral variations in carbonatitic systems due to extensive sampling campaigns and the provision of available drill core material. This study advances the knowledge and understanding of the deep and shallow emplacement and evolution of these carbonatites and their associated REE mineralizations.

1.5 Regional geology of the studied complexes

1.5.1 Palabora Carbonatite Complex (PCC)

Palabora represents a tripartite pipe-like (kidney-shaped) igneous complex of Proterozoic age (2060 Ma; Reischmann, 1995), which intruded the Archean granite-gneiss basement of the north-eastern Kaapvaal Craton (Wu et al., 2011). The complex covers an area of about 12 km² next to the city of Phalaborwa (Limpopo Province, South Africa). The intrusion is dominated by different types of pyroxenite and is divided into a northern and southern pyroxenite, and the central Loolekop pipe. Only the latter comprises a 1.3 x 0.8 km sized circular structure consisting of carbonatites and phoscorite.

Phoscorite (FOS), for which Palabora represents the type locality, is strongly interwoven with banded carbonatite (BCB). This association, in turn, is transected by a transgressive carbonatite (TCB). Newly discovered carbonatite veins, of increasing frequency with increasing depth, indicate another (hidden) carbonatite body in the centre of the southern pyroxenite. Carbonatites of the PCC are generally sövitic. Marginal zones of the pyroxenite intrusion (dominantly micaceous pyroxenite, MPY) experienced an interaction with the basement during emplacement that resulted in the formation of a feldspathic pyroxenite (FPY). The surrounding basement was fenitized (Fenite - FEN). Within the immediate vicinity of the complex syenites intruded as satellite bodies, and dolerite dykes (mostly Proterozoic; Wu et al., 2011) crosscut the entire region. Correlations to the extrapolated sediment cover yielded an emplacement depth of about 15 km (Eriksson, 1982), which defines the PCC one of the deepest known carbonatite complexes world-wide. Furthermore, it is suggested that the primary magma that formed the carbonatite complex was derived from an enriched mantle source and that the magma was generated by the same mantle plume activity that caused the formation of the Bushveld Complex (Wu et al., 2011).

The PCC is the only carbonatite world-wide that is primarily mined for copper. Besides copper, the complex is also mined for apatite and magnetite. Due to intensive mining over more than 50 years, the Palabora Mine represents one of the deepest open pit mines in the world. After reaching the maximum economic open pit depth in 2003, an underground mine was constructed. An intensive drilling campaign resulted in the complete sampling of a ~2000 m vertically continuous profile through the Loolekop pipe. Gravity data expands the continuity of subsurface data to a depth of at least 5 km (Eriksson, 1982).

1.5.2 Kaiserstuhl Volcanic Complex (KVC)

The KVC represents a Miocene (18-15 Ma; e.g., Kraml et al., 2006) volcanic to subvolcanic complex, which is situated in the Upper Rhine Graben, an area that is characterized by lithospheric thinning

(Bourgeois et al., 2007; Edel et al., 2006; Hüttner, 1996). Furthermore, the Upper Rhine Graben is featured by numerous partly deep-reaching listric and steep fault sets that are mostly subparallel to the graben geometry and typically form a horst and graben structure including variably sized tectonic blocks and relay ramps (e.g., Beccaletto et al., 2010).

The rocks of the KVC mainly consist of tephritic to phonolitic rocks, and minor nephelinitic, limburgitic, melilititic, haüynitic rock series (e.g., Baranyi et al., 1976; Braunger et al., 2018; Keller et al., 1990; Wimmenauer, 2003). Carbonatites emplaced in the centre of the complex (e.g., Schleicher et al., 1990; Wang et al., 2014) are exposed as four major carbonatite bodies (Badberg, Degenmatt, Haselschacher Buck, Orberg), and spatially associated with polygenetic breccias. Additionally, two smaller occurrences (<10 m in diameter) are situated at the Katharinenberg and Kirchberg. All carbonatite bodies are sövitic. Minor alvikitic and beforsitic dykes (cm- to m thick) crosscutting all rock types (Katz-Lehnert, 1989; Sommerauer and Katz-Lehnert, 1985). Field observations and geophysical data (Brauch et al., 2018 and references therein) identified dissection of the KVC by the regional Tuniberg normal fault, with a westwards down-throw of a vertical displacement between 1000 and 3000 m (Beccaletto et al., 2010; Groschopf et al., 1996). While the pipe-like Badberg carbonatite (400 m thick, inclined ~60° towards NW) shows no evidence to continue at greater depth, a continuous pipe-like system is indicated below the Degenmatt and Haselschacher Buck carbonatites (Brauch et al., 2018). Furthermore, the Badberg contains numerous cm- to m-sized rafts of calcite foidolites (xenoliths). Carbonatites at the Orberg display variable geometries including sills, sheet-like bodies and irregular cauliflower-like structures, that are strongly associated with polygenic breccias. These breccias probably promoted an intrusion into zones of weakness (Hubaux, 1964). At Henkenberg and Kirchberg alternating sequences of carbonatitic lavas, crystal tuffs and lapillistones (three 1 to 1.5 m thick layers, interbedded with silicate pyroclastics) are exposed (Keller, 1978; Keller, 1981; Keller, 1989). Due to historical test mining for Nb four boreholes with a depth between 100 to 500 m were drilled in the central KVC. Today the area is a protected natural habitat.

2. OBJECTIVES AND EXPECTED OUTPUTS

2.1 Studies on the main topic of this dissertation

Although carbonatites represent a high economic potential, their modes of emplacement, and the processes that cause variations in their mineralization, are not yet fully understood. However, the interest to understand such processes has increased significantly during the last years. Thus, our studies of the Palabora (South Africa) and Kaiserstuhl Complex (Southwest Germany) contribute to a better understanding of those carbonatitic systems, their emplacement and mineralization. Carbonatites from Palabora (e.g., Aldous, 1980; Eriksson, 1982; Hanekom et al., 1965; Palabora Mining Company, 1976; Wu et al., 2011) and the Kaiserstuhl (e.g., Braunger et al., 2018; Keller, 1981; Teiber et al., 2015; Walter et al., 2018; Wang et al., 2014; Wimmenauer, 2003) have been subject to previous investigations, but no detailed and systematic studies of mineralogy and mineral chemistry were available to date. Therefore, a comprehensive data set of the mineralogical inventory and the compositional variation of major minerals in carbonatites of these complexes is generated. In addition to a detailed textural, mineralogical and mineral chemical characterization of the carbonatites (and phoscorite), this thesis focuses on the following aspects of the individual studies.

2.1.1 The orthomagmatic, late-magmatic and post-magmatic REE mineralization, and its significance in carbonatites

Title of publication:
The Multistage REE Mineralization of the Palabora Carbonatite Complex, South Africa. (Study A)

This study is driven by the following major questions:

- How does the mineralogy, and especially the paragenetic sequence of REE minerals, change between the carbonatites and phoscorite?
- What are the different stages of formation and related processes that caused a distinct REE mineralization?
- Which processes caused a REE mineralization how effectively?
- How do different processes affect an existing REE mineralization?
- Which mechanisms lead to effective REE mineral alteration/REE redistribution?

2.1.2 The relationship of carbonatites and phoscorites based on phlogopite and apatite composition including a new emplacement model

Title of publication:
A model for the formation of carbonatite-phoscorite assemblages based on the compositional variation of mica and apatite from the Palabora Carbonatite Complex, South Africa. (Study B)

This study is driven by the following major questions:

- How are carbonatites (BCB and TCB), phoscorite and silicate rocks genetically related?
- Why were the carbonatites and phoscorites emplaced late into the silicate rock-dominated complexes?
- How do phoscorites form?
- Why do some carbonatite complexes lack any associated silicate rocks?
- Is it possible to create a petrogenetic model which explains the volumetric relationship between carbonatites, phoscorites and silicate rocks?

2.1.3 Mineralogical and mineral chemical variations in carbonatites due to magma-wall rock interactions

Title of publication:
Evidence for magma – wall rock interaction in carbonatites from the Kaiserstuhl Volcanic Complex (Southwest Germany). (Study C)

This study is driven by the following major questions:

- How does the mineralogy of the different carbonatite bodies of the KVC vary?
- Which features can be used to track contamination in carbonatites?
- How can we identify whether a silicate mineral in a carbonatite formed by (I) a pristine sufficiently high silica activity, (II) a change in silica activity by contamination, or (III) entrainment as a xenocryst?
- Are uncontaminated carbonatites capable of crystallizing higher amounts of silicates, especially mica?
- What effects does contamination by silicate-rich wall rocks have on the REE mineralization of carbonatites?

2.2 A co-authored publication on the petrogenetic significance of interactions with carbonatite-derived fluids

A further study contributed to the main topic of the thesis. It provided comparisons and additions to the above described publications (especially study A) in order to highlight the previous results and bring them into a broader context.

Title of publication:
Hydrothermal processes in the Fen carbonatite complex, southern Norway. (Study D)

This study sought to answer the following major questions:

- Which processes formed the mineralization of the Fen carbonatites?
- How do the different processes affect each other with respect to their mineralization?

3. RESULTS AND DISCUSSION

3.1 The orthomagmatic, late-magmatic and post-magmatic REE mineralization, and its significance in carbonatites

Title of publication:
The Multistage REE Mineralization of the Palabora Carbonatite Complex, South Africa. (Study A)

This study is based on a collection of about 400 drill core samples from 6 drill holes that combine to a vertical profile of about 2000 m. For analytical work 45 representative samples (20 TCB, 15 BCB, 10 FOS) have been chosen from the sample set. The samples were texturally investigated in much detail and all (10) relevant REE minerals and their different generations were analysed by electron micro probe

(341 analyses). The analytical data was primarily used to identify the different REE minerals and to distinguish different mineral generations by mineral composition. This distinction is based on a comparison of texturally characterized mineral phases and their mineral composition. Furthermore, this compositional distinction was especially important for mineral assemblages, where a clear textural distinction was not possible.

Our study has proven that phoscorites, and both carbonatite types (BCB and TCB) generally contain the almost same mineral assemblages in the same crystallization sequence, only modal abundances and textural features are variable. While phoscorites are dominated by early orthomagmatic minerals (e.g., olivine, apatite, phlogopite and magnetite), carbonatites commonly contain larger amounts of later orthomagmatic minerals (e.g., carbonates). The frequency of very early magmatic minerals (e.g., olivine and thorianite) and in general silicates (olivine and phlogopite) is higher in BCB than in TCB. A detailed investigation of the individual mineral generations and mineral assemblages has shown that the Loolekop has experienced four different evolutionary stages. This includes an orthomagmatic, a late-magmatic (hydrothermal), sulphide and post-magmatic (hydrothermal) stage, which can be observed in phoscorites as well as both carbonatites with a particularly strong late-magmatic effect on TCBs.

A combination of orthomagmatic and subsequent late-magmatic hydrothermal stages is typically observed in carbonatites of various complexes (e.g., Bear Lodge and Wicheeda; Moore et al., 2015; Trofanenko et al., 2016). Later hydrothermal post-magmatic stages are also common (e.g., Amba Dongar; Doroshkevich et al., 2009). Therefore, the individual evolutionary stages of carbonatites of the Palabora complex can be used as a generalized example for a typical formation and redistribution of REE minerals in carbonatitic systems, while, of course, compositional variation of the original magma and involved fluids can initiate relevant mineralogical differences. For this purpose, the different stages are first characterized and then compared with respect to their significance for the REE mineralizations.

The orthomagmatic stage is characterized by an early formation of forsteritic olivine, apatite, baddeleyite and thorianite, and first REE minerals (fergusonite and REE-Ti-betafite). However, the REE minerals are rare and form only small crystals. This mineral association is followed by the formation of phlogopite and the beginning of titanomagnetite crystallization coprecipitating with minor amounts of spinel and ilmenite. Additional spinel and ilmenite exsolved from titanomagnetite during cooling. The precipitation of Mg-rich calcite, which later exsolved wormlike dolomite, already started during the final stages of apatite formation, but its main crystallization stage took place relatively late in the crystallization sequence. Discrete dolomite crystallized during the intermediate stage of calcite formation. Contemporaneously to the main calcite crystallization, REE-, Ba- and Sr-carbonates such as bastnäsite, strontianite and barytocalcite formed. Furthermore, there are indications (see below) that carbocernaite and/or burbankite formed at this late orthomagmatic stage as is typical for other carbonatite complexes, but these phases were commonly replaced by later REE minerals (Wall et al., 1997; Zaitsev et al., 1998).

The late-magmatic stage is interweaved with the orthomagmatic stage and probably represents the result of an interaction of orthomagmatic minerals with a residual aqueous-carbonic fluid that was released by the carbonatite itself. This stage is characterized by a serpentinization of olivine and a replacement of olivine by chondrodite. The formation of serpentine or chondrodite certainly depends on the enrichment of F in the late-magmatic fluid, which in turn is most likely dependent on the mobilization of F by apatite dissolution. Furthermore, chloritization of orthomagmatic phlogopite, formation of secondary apatite and precipitation of tetraferriphlogopite (see study B) as well as monazite and britholite is observed. Monazite replaced apatite as thin rims or occasionally even completely by dissolution-reprecipitation reactions. Although orthomagmatic apatites incorporated significant concentrations of REE (Ø 8000 ppm), mass balance considerations demonstrate that these concentrations are not sufficient to provide enough REE for monazite precipitation. Therefore, an additional introduction of REE was essential for the formation of monazite. Britholite, in contrast, crystallized either at the expense of olivine, where it usually formed rims around olivine-serpentine/chondrodite assemblages, or less frequently in contact with phlogopite-chlorite assemblages.

Britholite was only rarely found as a discrete crystal in vein-like structures, where it occurs together with tetraferriphlogopite (see Study B). Usually, britholite occurrences worldwide indicate a primarily hydrothermal origin, replacing apatite or monazite and obtaining Si from the fluid itself (Budzyń et al., 2011; Uher et al., 2015). However, since britholite in Palabora was formed only after the provision of Si by the alteration of orthomagmatic silicates (olivine and phlogopite), it can be assumed that the mineralization fluid was originally low in Si and was only enriched during the alteration of silicates. The Si-enriched fluid might later form the discrete britholite crystals together with tetraferriphlogopite. As britholite mainly represents fluorbritholite-(Ce), it can also be assumed that the involved fluid must have been sufficiently enriched in F. Finally, the formation of a particular type of REE mineral was locally dependent on the availability of P or Si, provided by the alteration of orthomagmatic silicates or phosphates. Monazite is the dominant REE phase of this stage due to the high abundance of apatite and minor abundance of olivine.

Between the late-magmatic and the post-magmatic stage, a sulphide stage occurs. This sulphide stage is characterized by an injection of a sulphide-rich liquid which causes the extensive Fe-Cu sulphide mineralization of the Palabora complex. But, since this stage does not lead to an REE mineral formation or redistribution, it is not further discussed in this study. However, it should be mentioned that a corresponding inclusion of previous REE minerals (e.g., late-magmatic monazites and orthomagmatic REE-fluorcarbonates) in sulphide phases prevents alteration of these minerals by subsequent processes of the post-magmatic stage.

The post-magmatic stage caused a strong alteration of previously formed minerals (e.g., valleriitization of sulphides, recrystallization of carbonates) and a significant redistribution of certain elements (e.g., Sr and Th, but especially REE). Carbocernaite and/or burbankite are completely replaced by post-magmatic cordylite and ancylite, which are strongly associated with strontianite and baryte. Orthomagmatic bastnäsite is either replaced by a mixture of parisite, synchysite, strontianite and occasionally fluorite, or strongly dissolved with only few relicts that witness a former presence of bastnäsite. The alteration of late-magmatic REE minerals (dominantly represented by monazite) is also characterized by strong dissolution and (only for monazite) an additional replacement by a REE-poor apatite (mobilization of REE). Occasionally the formation of post-magmatic apatite at the expense of monazite is associated with the simultaneous formation of bastnäsite needles. It is suggested that this feature is caused by a REE oversaturation of the fluid during the remobilization of REE by alteration, and hence, indicates the fertility of the fluid. The remobilized element budget finally precipitates as a range of different REE minerals in carbonate veins due to fluid cooling. While the alteration of former REE phases can be seen as a proximal mineralization of the post-magmatic fluid, the recrystallization of the remobilized element budget in veins can be described as the corresponding distal mineralization. This distal mineralization is dominated by bastnäsite and ancylite, which are often associated with further secondary magnetite, strontianite (in absence of ancylite) and thorianite or thorite.

The formation of secondary Th minerals (thorianite and thorite) is typical for those hydrothermal low temperature mineralizations. Since Th was mobilized during the alteration of REE minerals (with certain amounts of Th), but also of primary Th minerals (e.g., orthomagmatic thorianite), and Th cannot easily be incorporated into secondary REE minerals at significantly lower temperatures (Budzyń et al., 2010; Doroshkevich et al., 2008; Read et al., 2002), Th precipitates as discrete Th minerals. This is evidenced by a comparison of mineral compositions of the different REE mineral generations and represents an important indicator to distinguish those mineral generations.

Finally, an important post-magmatic mineral of both proximal and distal mineralization is anzaite. The identification of anzaite in Palabora represents the second occurrence of anzaite [$REE_4FeTi_6O_{18}(OH)_2$] world-wide, with the type locality being the Afrikanda complex (Russia; Chakhmouradian et al., 2015). The formation of anzaite is dependent on the availability of Ti, which is obtained by the alteration of ilmenite. If REE are already sufficiently enriched in the fluid, ilmenite is simply replaced by anzaite (proximal mineralization). Otherwise, ilmenite is dissolved by the fluid and Ti is remobilized. Such a remobilization of Ti is usually ascribed to very low pH fluids containing sufficient F as complexing agent (e.g., Van Baalen, 1993). But those conditions are considered to be unlikely for the post-magmatic fluid. Alternatively, Manning (2004) pointed out that Ti can be transported by complexing agents of polymerized silicate molecules (e.g., Ti-aluminosilicate complexes; Beitter et al., 2008; Tropper and Manning, 2005). Since the post-magmatic fluid causes a strong valleriitization of sulphides and precipitation of serpentine (independent on the presence of silicate minerals), which both require a certain concentration of mobilized Al and Si, respectively, it can be concluded that adequate amounts of these complexing agents are available. A direct indication is the rapid sequential formation of valleriite (consumption of Al), serpentine (consumption of Si) and subsequent precipitation of anzaite by the loss of complexing agents.

Since the post-magmatic fluid did not cause an intensive alteration of pre-existing silicate phases, but caused a significant formation of serpentine and tetraferriphlogopite, it can be assumed that this fluid was, in contrast to the late-magmatic fluid, already enriched in Si. On the other hand, the strong alteration and dissolution of orthomagmatic and late-magmatic REE minerals, and remobilization of REE instead of precipitation, indicates that the involved fluid was originally low in REE and was only enriched during the alteration of REE minerals. A comparison of the late-magmatic and post-magmatic fluid further reveals the importance of the late-magmatic fluid to initiate the REE mineralization of Palabora. The post-magmatic fluid, in contrast, caused an effective alteration of pre-existing mineral phases and redistribution of REE minerals due to remobilization and reprecipitation processes.

The lack of REE in olivine and low/insufficient REE content in apatite (see above) reflects the necessity to import REE into the system during the late-magmatic stage to precipitate REE minerals (britholite and monazite). While not only late-magmatic, but also late orthomagmatic REE minerals were altered during the post-magmatic stage, early orthomagmatic REE minerals were frequently preserved in subsequently formed mineral phases (e.g., magnetite), similar to REE minerals enclosed in sulphides (see above). Nevertheless, it should be noted that, very similar to what is observed in other carbonatite complexes, due to its high modal content, apatite represents the main REE host at the PCC (Dawson and Hinton, 2003). However, the economic character of a carbonatite is dependent on the occurrence of discrete REE minerals (e.g., bastnäsite and monazite) due to the processability of these mineral phases.

3.2 The relationship of carbonatite and phoscorite magmas during emplacement based on phlogopite and apatite mineral chemistry including a new emplacement model

Title of publication:
A model for the formation of carbonatite-phoscorite assemblages based on the compositional variation of mica and apatite from the Palabora Carbonatite Complex, South Africa. (Study B)

This study is based on the same sample set that was used in study A and the same selected samples were analysed in this study. In addition, we added three samples of associated silicate rocks (2 MPY, 1 FEN). As mica and apatite occur as major constituents in all rock types of the Loolekop deposit, textural and mineral chemical variations in these minerals are used to shed light into the relations between the different lithologies. For this approach about 450 mica and 550 apatite electron micro probe analyses were acquired.

Mineral chemical analyses have shown that 5 different types of mica can be distinguished in the carbonatites (TCB and BCB), phoscorite and silicate rocks at Palabora. These types include common phlogopite (Fe^{2+}-poor; type I), mica of the phlogopite-kinoshitalite ($K^{+}+Si^{4+}\leftrightarrow Ba^{2+}+{}^{IV}Al^{3+}$; type II), phlogopite-eastonite ($Mg^{2+}+Si^{4+}\leftrightarrow {}^{VI}Al^{3+}+{}^{IV}Al^{3+}$; type III), phlogopite-annite series/biotite ($Mg^{2+}\leftrightarrow Fe^{2+}$; annite component >20%; type IV), and tetraferriphlogopite (${}^{IV}Al^{3+}\leftrightarrow {}^{IV}Fe^{3+}$; type V). Mica of type I-IV are interpreted to be of magmatic origin, whereas tetraferriphlogopites (type V) indicate a late-magmatic hydrothermal origin. Our study pointed out that the different types of mica are limited to specific rock types (except tetraferriphlogopite). Type I mica occur exclusively in BCB and FOS. Type II mica exclusively occur in TCB. Mica type III is limited to sections of BCB and FOS that are in contact or close to a contact to TCB and were interpreted as a product of an interaction with TCB melt. Mica type IV (biotites) exclusively occur in pyroxenites. This is in accordance to mica composition of other carbonatite complexes, where silicate rocks are associated with carbonatitic rocks and biotite exclusively occur in the silicate rocks (e.g., Brod et al., 2001). Tetraferriphlogopites (mica type V) typically occur in late-stage rocks, crystallizing at lower temperatures (Fleet, 2003; Lee et al., 2003), forming rims with sharp compositional changes to pre-existing phlogopite cores (e.g., Brod et al., 2001) or completely new individual crystals (e.g., Lee et al., 2003). Tetraferriphlogopite from Palabora crystallized as new individual crystals in veins, where it is occasionally associated with aggregates of (rarely euhedral) britholite and apatite-monazite dissolution structures (see study A) that are both aligned parallel to the vein-like orientation of tetraferriphlogopites. Hence, it is assumed that tetraferriphlogopite, britholite and monazite formed contemporaneously during the late-magmatic stage (study A) in TCB, BCB and FOS, decoupled from the orthomagmatic mica formation.

The majority of apatites (in FOS, BCB and TCB) depicts a large compositional overlap with generally low concentrations of REE, Si, Sr and Na (all <0.05 apfu) and are interpreted to be orthomagmatic. In contrast, there are a few outliers exhibiting higher REE concentrations (up to 0.15 apfu), which are suggested to represent late-stage apatites. The REE enrichment results from different coupled substitution mechanisms, namely britholite substitution ($P^{5+}+Ca^{2+}\leftrightarrow Si^{4+}+REE^{3+}$ in FOS and few BCB) and belovite substitution ($5Ca^{2+} \leftrightarrow Na^{+}+3Sr^{2+}+REE^{3+}$ in BCB and TCB), which probably dependent on the availability of Si and Sr in late-stage fluids. Interestingly, these outliers occur in samples which are characterized by the occurrence of late-stage mica type V (tetraferriphlogopite) and hence confirm the assumption of study A that late- magmatic fluids introduced a REE mineralization.

In this terms, the compositional variations of both, phlogopite and apatite reflect the multistage evolution of the Loolekop deposit, with the availability of Al being a prominent factor controlling the mica composition. However, neither phlogopite nor apatite show systematic compositional changes with depth (over a profile of >2000 m), which evidences the absence of a vertical zonation. Furthermore, the obtained data point out that compositional variations in mica are much more useful to reconstruct magmatic differentiation processes than apatite at Palabora. Magmatic apatites plot unsystematically in a defined cloud without clear indications, with respect to composition. Additionally, the distinct mica compositions provide information about the relations between the different rock types at Palabora.

The nearly identical mica mineral chemistry of BCB and FOS, their identical mineralogy but different modal composition (see study A) and strong structural relations (strongly intercalated into each other) indicate a genetic dependence of these rock types. While fractional crystallization cannot explain an analogous compositional development of mica in BCB and FOS, liquid immiscibility seems to be the most likely process that might have formed the phoscorite. This has also been described from other carbonatite-phoscorite associations (e.g., Catalão I+II, Sokli; Brod et al., 2001; Lee et al., 2003). Further observations on other carbonatite-phoscorite complexes strengthens the assumption that liquid immiscibility plays a key role for phoscorite formation. Those observations include orbicular and spherulitic phoscorite fractions in carbonatites and vice versa (e.g., Krasnova et al., 2004b; Lapin and Vartiainen, 1983) and studies of mineral inclusions in olivine and apatite (Mikhailova et al., 2002). Melt inclusions evidence that the parental magma of some carbonatites was enriched in Fe and/or P (e.g., Chen et al., 2013; Guzmics et al., 2008; Krasnova et al., 2004b). Phoscorites, in turn, contain melt inclusions dominated by various carbonates (Veksler et al., 1998; Zaitsev and Kamenetsky, 2013). In contrast, TCB as well as associated silicate rocks (MPY, FEN) reflect a completely different mica composition, which indicates a separate evolution of these lithologies with TCBs representing a higher evolved carbonatite magma compared to BCB.

Anyhow, the assumption that carbonatite-phoscorite associations are formed by liquid immiscibility raises the question of a parental magma, its origin and mode of intrusion. Furthermore, it is of utmost interest to compare the variable ratios of carbonatites and phoscorites between different complexes in order to point out dependencies, e.g. with depth. Interestingly, a few studies have shown that there is a depth dependency between the proportions of carbonatites and silicate rocks (Arzamastsev et al., 2000) as well as certain mineralogical variations (Frolov, 1971). But individual mechanisms are only unsatisfactorily known. This has driven us to develop a model based on the existence of a parental melt for carbonatites and phoscorites, which explains the rock associations in carbonatite complexes. For this purpose it must be considered that previous isotope studies indicate that neither fractional crystallization nor liquid immiscibility can be attributed to the formation of associated silicate rocks and carbonatites/phoscorites at Palabora (Eriksson, 1982). Accordingly, we suggest a contemporaneous emplacement of both lithologies but no genetic link between them. Such genetic independence of spatially associated carbonatites and silicate rocks in alkaline complexes is frequently suspected (Gittins and Harmer, 2001).

We suppose that carbonate-rich melts that are generated in the lithospheric metasomatized mantle at depths >70 km (e.g., Wyllie and Lee, 1998) by low degree partial melting (<5%; e.g., Dasgupta et al., 2007; Gudfinnsson and Presnall, 2005) are enriched in Fe and especially in P (in the upper mantle) due to the preferred partition of these elements into carbonatites (Jones et al., 1995; Lindsley and Epler, 2017; Naslund, 1983). A remixing with silicate melt is prohibited by the liquid immiscibility, which further supports the separation of these two melts. The enrichment of Fe and P finally forms carbonate-phosphate/iron-oxide-rich (CPIO) melts, which can be considered as the required parental melts for carbonatites and phoscorites. The pristine carbonatite melt provides a buoyancy due to its low densities (typically 2.2-2.6 g/cm^3; e.g., Dobson et al., 1996; Genge et al., 1995; Kono et al., 2014; Wolff, 1994) within the much more voluminous silicate melt accumulation. But by the enrichment of Fe and P the CPIO melt becomes increasingly denser, resulting in a loss of buoyancy and a state of density equalization. As a result of a depressurization-related magma ascent, the CPIO melt is dragged together with the silicate melt into an ascending channel (activated weakness zones) and introduced into crustal levels. The introduction timing (relative to the first introduction of silicate melt) is dependent on the distance between the CPIO melt body and the ascending channel. Therefore, these channels were commonly already passed by silicate magma prior to the intrusion of the CPIO melt. Due to decreases in temperature and pressure during ascent, a Fe and P-rich melt (phoscorite) and carbonate-rich melt (carbonatite) finally segregates from the CPIO melt. This segregation can additionally be supported by the presence of larger quantities of F in the parental melt (Hou et al., 2017). Lindsley and Epler (2017) pointed out that discrete iron-oxide melts (low in Ti) are not stable below 1000 °C even in the presence of fluxes such as P, F and C. It must, therefore, be assumed that the phoscorite melts starts to crystallize very soon after segregation, which is additionally supported by the fact that C is generally the most important flux (Lindsley and Epler, 2017) and remains in large quantities in the carbonatite magma during segregation. Hence, it can be assumed, that larger quantities of phoscorite only occur in relatively deep emplacement depth, where segregation took place. Medium to shallow emplacement depth of carbonatite complexes may consequently be characterized by rather low amounts or complete absence of phoscorites, which is confirmed by the absence of any extrusive phoscorites (Krasnova et al., 2004b). The simultaneous/directly subsequent crystallization of early carbonatite (e.g., BCB) causes the typical intercalation with phoscorite, while crystal fractionation produces higher evolved carbonatite magmas (e.g., TCB). The segregation and differentiation processes initiate a substantial density contrast between the high density phoscorite and low density carbonatite melts, which may cause a “jet-like” ascent of the residual carbonatite melt. Since silicate melts have relatively high viscosities and higher solidus temperatures in contrast to carbonatitic melts, their magma activity may already have ebbed in certain crustal levels. Rapidly ascending extremely low viscose carbonatites (Treiman and Schedl, 1983) may pass through those silicate magma fronts ascending to higher emplacement levels, where the intruding carbonatite magma forms carbonatite complexes without a silicate rock association. About 20% of carbonatite occurrences reflect such silicate rock-free complexes and, confirmatively, most of them represent rather shallow intruded carbonatites (Woolley and Kjarsgaard, 2008). However, it must be noted that the sequence of characteristic carbonate-phoscorite-silicate rock ratios in certain emplacement depths can be variable. These ratios strongly dependent on factors such as crustal thickness, geological setting (e.g., inter-cratonic or rift zone) and the timing of silicate magma chamber formation within the crust. The typical sequences of rock associations in carbonatite complexes are thus controlled by the source-emplacement-distance (ΔS-E).

In this context, it can be assumed from our generalized model that deeper crustal regions, relatively close to the melt source (low ΔS-E), are characterized by higher volumetric proportions of ultramafic silicate rocks and lower amounts of carbonatitic rocks. Additionally, these complexes display a relatively high phoscorite-carbonatite ratio. Conclusively, an increase of the ΔS-E entails a decrease in phoscorite-carbonatite ratios, and a decrease in silicate-carbonatite ratios, until the carbonatite proportion of a complex exceeds the silicate proportion and finally pure carbonatite complexes occur.

3.3 Mineralogical and mineral chemical variations in carbonatites due to magma – wall rock interactions

Title of publication:
Evidence for magma – wall rock interaction in carbonatites from the Kaiserstuhl Volcanic Complex (Southwest Germany). (Study C)

This study is based on a collection of about 400 surface outcrop and drill core samples (2 historic drill holes). For analytical work 48 representative samples have been chosen from the sample set. A detailed textural investigated was carried out and all major minerals and relevant minor minerals were analysed by electron micro probe (apatite [N≈520], mica [N≈620], magnetite [N≈260], carbonates [N≈380], clinopyroxene [N≈130], garnet [N≈200], olivine [N≈36], monticellite [N≈19]). The selected samples represent the four major (Badberg, Degenmatt, Haselschacher Buck and Orberg) and one minor (Katharinenberg) intrusive carbonatite bodies, as well as two extrusive carbonatite occurrences (Henkenberg and Kirchberg). The analytical data was used to identify compositional variation in minerals of the different carbonatite bodies.

Since mica and apatite are typically used to indicate different processes within carbonatitic systems (e.g., see study B) we used these minerals to reveal processes that are in relation to the mineralogical variations between the carbonatite bodies of the KVC. Macroscopically, the Badberg carbonatites differ from the other KVC carbonatites due to the presence of cm- to m-sized silicate rock inclusions (xenoliths), which can be best described as calcite foidolites. Furthermore, the Badberg is the only carbonatite body of the Kaiserstuhl that contains clinopyroxene. In general, besides calcite, the coarse grained calcite carbonatites of the Kaiserstuhl contain, apatite, mica, variable amounts of spinel group minerals of the magnesioferrite-magnetite series, pyrochlore, occasionally olivine (Katharinenberg and Haselschacher Buck only), monticellite (Orberg only), zirconolite (Haselschacher Buck only) and a range of sulphides (trace minerals).

Similar to the Badberg, also some extrusive carbonatites (crystal tuffs) of the Henkenberg location include xenolitic calcite foidolites. Other extrusive carbonatites contain xenocrysts of nepheline (lava from Kirchberg), garnet (lava from Kirchberg, lapillistones and crystal tuffs from Henkenberg) and clinopyroxenes (lapillistones and crystal tuffs from Henkenberg).

Calcite foidolite (xenolith) itself contains large amounts of a mixture of various zeolite minerals, calcite, mica and other minerals that have almost completely replaced (post-magmatically) former foid minerals (nosean or haüyne). In addition, relicts of alkali feldspar can rarely be observed. Relictic garnet cores occur enclosed in anhedral masses of recrystallized garnet, while clinopyroxenes have been completely recrystallized as subhedral and interstitial grains. Since most minerals of the calcite foidolite are completely replaced or recrystallized, it is difficult to identify its protolith. However, a comparison of relicts of the original garnet with the garnet composition of other KVC rock types indicates that nosean syenite represents the most probable candidate. The occurrence of alkali feldspar relicts, foids and clinopyroxene confirm this suggestion. Furthermore, those nosean syenites directly underlay the tilted Badberg body.

The contact between carbonatite and the enclosed calcite foidolites is characterized by a black-wall-like seam of coarse-grained khaki to olive-green mica. This mica seam occasionally surrounds a transition zone (outer rim of calcite foidolites) that is characterized by strongly altered clinopyroxene and garnet and high proportions of calcite, which typically intruded as carbonatitic veins into the xenoliths. This contact indicates at least a marginal resorption of the calcite foidolites by the carbonatitic magma, which is accompanied by a metasomatic alteration of the remaining xenoliths and has caused the recrystallization of corresponding minerals (see above). A resorption of xenoliths is further indicated by an increasing disaggregation of xenoliths in a margin-centre profile of the pipe-like structure of the Badberg carbonatite. This feature could be assigned to a longer persisting heat flow in the central area and an earlier cooling in the marginal zones of the carbonatite pipe.

In addition to the stubby coarse-grained black wall mica, which occasionally covers large portions of the carbonatite around the xenoliths, the Badberg carbonatite also contains large-sized bundles of mica laths that occur independently of the presence of silicate rock xenoliths. Although these two types of mica in the Badberg carbonatite differ slightly in their composition, they are, as a whole, clearly separated texturally and compositionally from micas of the other carbonatite occurrences of the KVC. While the Badberg is commonly very mica-rich, with mica up to a size of 2 cm, the other locations are generally mica-poor and contain significantly smaller mica crystals (<2 mm). Compositionally, mica of the Badberg differs from mica of the other KVC carbonatites mainly by a considerably higher Fe^{2+} and increased Mn content. In general, mica of the Kaiserstuhl is characterized by a combination of the kinoshitalite ($K^+ + Si^{4+} \leftrightarrow Ba^{2+} + {}^{IV}Al^{3+}$) and eastonite substitution ($Mg^{2+} + Si^{4+} \leftrightarrow {}^{IV}Al^{3+} + {}^{VI}Al^{3+}$). Most micas (with exception of the Badberg) are dominated by the kinoshitalite substitution. Badberg mica, in contrast, is dominated by the eastonite substitution. This indicates an excess of Al over Ba in the Badberg carbonatite.

Apatites also depict a strong variability between carbonatites of the Badberg and other KVC localities. The composition of Badberg apatite cores is very similar to the apatite composition of the other carbonatite localities and differs only by an increased Sr content (with few Orberg apatites also have an increased Sr content). In contrast, the composition of Badberg apatite rims differs strongly from those of the other apatites. These rims experienced a strong britholite substitution ($Ca^{2+} + P^{5+} \leftrightarrow REE^{3+} + Si^{4+}$) and thus an enrichment of REE. This enrichment increases further from the margin to the centre of the pipe-like structure of the Badberg carbonatite. In contrast, some Orberg apatites show an increased concentration of Na and a subordinate belovite substitution ($2Ca^{2+} + (3Ca^{2+}) \leftrightarrow REE^{3+} + Na^+ + (3Sr^{2+})$). This belovite substitution is also responsible for the above-mentioned enrichment of Sr in Orberg apatites. However, since magmatic processes shall be discussed and a belovite substitution in apatites is predominantly assigned to hydrothermal processes (e.g., de Toledo et al., 2004; Doroshkevich et al., 2009), this should not be considered for now. A pronounced britholite substitution (0.3-0.5 REE+Si pfu) in apatite, in contrast, is not possible in hydrothermal stages (Anenburg et al., 2018; Anenburg and Mavrogenes, 2018) and is attributed to a magmatic phase (>600 °C). A hydrothermal overprint at these high REE contents (4-6 wt.% REE_2O_3) would have led to the formation of REE-poor apatites and discrete REE minerals. In the presence of sufficient Si e.g. cerite (e.g., Anenburg et al., 2018; Anenburg and Mavrogenes, 2018) and in the absence of Si e.g. monazite would have formed (e.g., study A).

In contrast to the enrichment of Sr in apatite, which indicates a higher magmatic evolution (by magmatic differentiation; of the Badberg with respect to the other localities), the sharp contact between core and compositionally variable rim argues against magmatic differentiation as a mechanism for Si and REE enrichment in the rim, for which a continuous transition in mineral chemistry would be expected. Likewise, the increased occurrence of mica and the exclusive occurrence of clinopyroxene in the Badberg carbonatite cannot be explained by magmatic differentiation, since silicates crystallize in carbonatites quite early and accordingly deplete the magma in SiO_2 by fractionation. All available evidence suggests that the variability of Badberg mineralogy and mineral chemistry depends on the inclusion of calcite foidolites, and the more these calcite foidolites are resorbed and metasomatized, the larger the variability.

A comparison of mineral compositions of the calcite foidolite with mineral composition of the KVC nosean syenite (protolith) demonstrates that certain amounts of Si, Al, K, Fe and Ti must have been released during the replacement of alkali feldspar by foids and the recrystallization of clinopyroxene and garnet. On the other hand, certain amounts of Ca and Mg as well as smaller amounts of Nb and Zr are consumed. This indicates an interaction between the xenoliths and the carbonatitic melt and may explain an abrupt availability of elements that cause corresponding mineral chemical variations in mica (observed at the Badberg). Nevertheless, it remains the question if mineralogical variations were also caused by contamination and thus the increased occurrence of mica and clinopyroxenes in Badberg can be explained.

In general, different silicates are described in carbonatites worldwide (e.g., Reguir et al., 2012), while their presence is strongly dependent on silica activity, which is generally very low in carbonatites (Barker, 2001; Massuyeau et al., 2015). Three main types of silicates are distinguished in carbonatites (modified after Barker, 2001): (1) primary crystallized silicates, which are (a) either formed by sufficient Si in the original melt or (b) by a supply of Si (e.g., by contamination), (2) xenocrysts and (3) subsolidus phases. According to experimental constrains, which suggest a low solubility of Si and Al in carbonatites (<2.9 wt.% SiO_2, <1 wt.% Al_2O_3; Brooker and Kjarsgaard, 2011; Weidendorfer et al., 2017), mass balance calculations based on carbonatite melt densities (2.2-2.6 g/cm³; e.g., Dobson et al., 1996; Genge et al., 1995; Kono et al., 2014; Wolff, 1994) and typical Al and Si contents of mica indicate that a maximum modal amount of about 7 % can be expected to crystallize from a carbonatite without additional Si influx. Textural features of mica (black wall seams around xenoliths and bundles of long, occasionally filigree laths) indicate an in-situ formation. Compositional overlaps with clinopyroxene from calcite foidolites and structural evidence that clinopyroxene in carbonatite is not a xenocryst of the calcite foidolite (euhedral in carbonatite, anhedral in calcite foidolites), as well as the absence of small-scale compositional changes (zoning) further indicate an in-situ formation of clinopyroxene in the carbonatite. Therefore, neither mica nor clinopyroxene are xenocrysts, but both are crystallized by Si-contamination (silicate type 1b, see above).

This contamination also had a strong effect on apatite. The higher the silica input, the higher the incorporation of Si into apatite and thus the consumption of REE based on britholite substitution (e.g., Hammouda et al., 2010). Furthermore, experimental data (Klemme and Dalpé, 2003) confirm a pronounced partitioning of REE into apatite with increasing SiO_2 content in the melt.

A comparison of main REE-bearing minerals (apatite and pyrochlore) between the Badberg and other KVC carbonatites has shown that the contamination process has significantly influenced the REE distribution at the Badberg. Most pyrochlore of the KVC carbonatites (with exception of the Badberg) experienced a late-stage hydrothermal overprint, which strongly enriched this pyrochlore in REE (Walter et al., 2018), whereas the pyrochlore of the Badberg is largely unaffected. This phenomenon may be attributed to an early consumption of REE by the contamination-induced britholite substitution in apatite and thus to a limited availability of REE in late stages. This is in accordance with the occurrence of relatively REE-poor apatite in the coarse grained calcite carbonatite, where pyrochlore was hydrothermally enriched in REE.

3.4 A co-authored publication on the petrogenetic significance of interactions with carbonatite-derived fluids

Title of publication:
Hydrothermal processes in the Fen carbonatite complex, southern Norway. (Study D)

The Fen carbonatite complex experienced at least three different hydrothermal alteration events. Besides a sulphide-rich fluid (fluid 1) that was most likely derived from associated mafic silicate rocks, a REE-rich fluid (fluid 2) and a Si-rich fluid (fluid 3) modified the original mineralogy of the Fen complex. The REE-rich fluid was most likely derived from the carbonatites and represents an autometasomatic fluid. The Si-rich fluid represents most probably an oxidizing meteoric fluid that was in equilibrium with the basement. An interaction of the REE-rich and Si-rich fluids caused an intense alteration of the carbonatites and the formation of the famous rødberg.

Fluid 1 induced a widespread pyrite formation that can be found in all lithologies. Occasionally massive pyrite veins cross-cut the carbonatites. Fluid 2 caused a remobilization and redistribution of Fe and Al and formation of discrete REE minerals dominated by REE-fluorcarbonates. Minor amounts of allanite, monazite, samarskite and aeschynite can be identified. Fluid 3 induced a partial silicification of the carbonatite and an unusual mobilization of phosphorus by the replacement of apatite by quartz, resulting in the formation of apatite and monazite veins. A mixing of fluid 2 and 3 finally caused the formation of iron ores (hematite). A remobilization of preferentially LREE by fluid 3 from pre-existing minerals (formed by fluid 2) resulted in the relative enrichment of HREE in some altered portions of the complex. There are evidences that Nb and Ti were transported together with REE in the evolved carbonatitic fluid. Furthermore, mineral associations and enrichment of Th together with HREE indicate similar behaviour of these elements during the hydrothermal alteration of the carbonatites.

4. SUMMARY, CONCLUSIONS AND IMPLICATIONS

Our studies have demonstrated that carbonatites may be formed by, and modified by, a variety of different processes that may result in wide variability in both mineralogy and mineral chemistry. The REE mineralization of carbonatites may strongly vary as a function of the absence or involvement of relevant mineralising processes as well as their intensity. In fact, orthomagmatic processes within a carbonatite body cause the weakest variations and a subordinate formation of REE minerals. Early orthomagmatic REE mineralizations typically consist predominantly of REE-Ti/Nb oxides (e.g., pyrochlore group minerals; study A & C). Minor REE-Zr phases (e.g., zirconolite; study C) can crystallise. Frequently, those early (small sized) mineral phases are included into later crystallizing (much larger) mineral phases and thus often protected from later alteration (study A). Furthermore, REEs are incorporated in apatites and despite their low REE content, apatites may significantly contribute to a whole rock REE enrichment due to their high modal proportions. Late orthomagmatic phases mainly occur as REE carbonates (e.g., bastnäsite, synchysite, parisite, burbankite and carbocernaite; study A). Additionally monazite is occasionally described as an orthomagmatic phase (e.g., at Mountain Pass; Castor, 2008). REE may also be incorporated into carbonates (e.g., calcite, dolomite). Even if these carbonates contain rather lower contents of REE, the REE budget of a carbonatite may, similar to apatite, be strongly affected by carbonates due to their high modal content.

Carbonatites are typically associated with phoscorites in several complexes and a genetic relationship can be traced by mineral compositional variations, especially in mica (study B). Apatites, on the other hand, are rather poor indicators for such relations, at least at Palabora, as they do not reveal systematic variations. Instead apatites indicate hydrothermal variations (see below). Neither mica nor apatite depict depth-dependent systematic variations over a vertical profile of 2000 m, which reflects a lacking zonation over this range. This is confirmed by a non-varying depth profile of 1550 m at Kovdor (Krasnova et al., 2004a). Nevertheless, mica composition emphasizes that the carbonatite-phoscorite association must have been formed by liquid immiscibility, due to the segregation of their parental mantle melt (study B). Consequently, phoscorites are mainly present in deeply emplaced carbonatite complexes. Carbonatites and phoscorites show a nearly identical mineralogy, which differs only in the modal composition. This is also valid for the REE mineralization. Similarly, mineral composition differs only negligibly. However, due to the very high apatite modal content in phoscorites, REE are primarily incorporated in apatite, with a subordinate occurrence of later formed discrete REE mineral phases.

Globally, the orthomagmatic REE mineralization of carbonatites (as well as phoscorites) is not economically relevant with exception of the Mountain Pass carbonatite (e.g., Castor, 2008). In contrast, hydrothermal late-magmatic and post-magmatic processes play a much more important role in the enrichment of REE in carbonatites. In particular, late-magmatic hydrothermal processes are responsible for an enhanced introduction of REE and corresponding REE mineralization. At Palabora, this resulted in crystallisation of discrete REE minerals at the expense of pre-existing non-REE phases. Additionally, these processes occasionally lead to a modification of apatite (REE enrichment) and to the formation of Al-poor mica. The mineralizing late-magmatic fluid probably originates from the carbonatite itself. Those fluids represent most likely the most common sources for a deposit-quality enrichment of REE-minerals in carbonatites (e.g., Wall and Mariano, 1996). The most common REE minerals are monazite and britholite (study A). Allanite and occasionally REE-carbonates are also known from other carbonatite complexes (e.g., Fen, study D).

Another hydrothermal stage is the post-magmatic stage, which induced a strong alteration of the pre-existing mineral content and a redistribution especially of the REE. Both orthomagmatic and late-magmatic REE minerals are affected by this alteration and redistribution processes, which form proximal and distal mineralizations. While the proximal mineralization involves alteration or direct replacement of pre-existing minerals, distal mineralization depends on effective mobilization of relevant elements and a subsequent reprecipitation. The most common REE minerals of this stage are REE-carbonates (bastnäsite, synchysite, parisite, ancylite, cordylite; study A), as a feature for the Palabora complex additionally anzaite occurs. Due to the strong dependence on the pre-existing mineralogy, an enhanced mobilization, enrichment and redistribution of REE minerals within variable local chemical (micro) environments only occurs if the previous stages have formed appropriate REE phases.

On the other hand, the late-magmatic stage can only provide notable REE mineralization if enough REE has been enriched in the related fluid. This is of course dependent on the partition of REE (and other relevant elements) between the residual melt and the fluid. An enrichment of REE in a carbonatite melt of the late orthomagmatic stage, in turn, depends on the removal of REE by early orthomagmatic minerals. In this context, particularly apatite may play an important role (see above).

Similar to the Palabora complex (study A), carbonatites of the Fen complex (study D) also experienced an intense hydrothermal overprint. Involved fluids of both complexes are similar in some aspects. Both complexes contain REE-rich carbonatite-derived fluids that formed the main REE mineralization. Both complexes contain a Si-rich fluid that caused a significant alteration of pre-existing minerals, and a mobilization and redistribution of their element budget. Although no information could be provided about the origin (certainly not a meteoric) of the post-magmatic fluid of Palabora, an external fluid origin in equilibrium with the basement could be possible (similar to the Fen complex). Nevertheless, the intense hydrothermal overprint of the carbonatites made Fen the biggest carbonatite-related REE and Th deposit in Europe.

The Kaiserstuhl, in contrast, shows an almost absent REE mineralization in the late-magmatic stage of the Badberg body, but a significant REE enrichment in apatite (study C). In contrast, other carbonatite bodies of the KVC (Orberg, Degenmatt, Haselschacher Buck) lack an enhanced REE enrichment in apatite, but reveal a late magmatic hydrothermal modification (including REE enrichment) of pyrochlore

(Walter et al., 2018). We assign this variation to a contamination of the Badberg by silicate rocks, where a britholite substitution and related REE enrichment in the apatite was promoted during the orthomagmatic stage. This further inhibited later enrichment of REE in residual liquids/fluids and emphasizes the potential importance of contamination of carbonatitic magmas for REE mineralizations. In general, contamination in carbonatites is typically very poorly identifiable by means of radiogenic isotope (e.g. Sr, Nd) data, as their isotope systems are "buffered" (due to high concentrations) against contamination with silicate rocks (usually much lower concentrations of these elements; e.g., Bell and Tilton, 2002). Furthermore, it is assumed that carbonatites are not specifically prone to contamination by crustal or cogenetic intrusive rocks, as low densities and extremely low viscosities of carbonate melts allow a rapid ascent (e.g., Jones et al., 2013; Treiman and Schedl, 1983) without a notable melt-rock interaction. However, based on textural observations and compositional variations of mica and apatite, we were able to verify a related contamination of the Badberg carbonatite. This indicates, as Study B has already shown, that mica especially, but also apatite (under certain conditions), can be effectively used as geochemical indicator in carbonatitic systems. In addition, it also demonstrates the basically sensitive behaviour of REEs.

In conclusion, it can be assumed that one important candidate for an ideal REE enrichment of high economic significance is a carbonatite which has not experienced any contamination, contains only minor amounts of apatite, experienced a strong enrichment of REE by a late magmatic fluid, and finally completed a redistribution and enrichment of REE by external fluids. Such characteristics may be most likely expected from highly differentiated carbonatites that intruded shallow crustal levels and consequently lack associated phoscorites, but did not intrude into tectonically active areas where entrainment of silicate wall rock fragments is promoted. As an absolute optimum process for REE concentration, carbonatites need to be altered by supergene enrichment to laterites. Further work on this topic should focus in particular on the potential fluid phases that induce the crystallisation of discrete REE minerals. For carbonatites, neither the influence of different natural fluid types on the REE mineralization nor the influence of different processes on the fluid composition is sufficiently known. Additionally, as contamination in carbonatitic systems reflects a previously unnoticed effect, it is necessary to investigate such processes and their influences in further case studies to determine differences due to variable rock compositions (e.g. BIF, gabbro, etc.).

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