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New Insights on the Rare Earth Element Mineralisation of the Storkwitz Carbonatite, Germany

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Running title: NEW INSIGHTS INTO REE MINERALISATION AT STORKWITZ CARBONATITE

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Abstract

The Storkwitz carbonatite breccia, located near Delitzsch, Germany, is one of the few European domestic rare earth elements (REE) deposits but it is relatively understudied owing to more than 100 m of Cenozoic sedimentary cover. We present the results of a petrological investigation of the recently acquired ~700 m deep SES 1/2012 borehole. The Storkwitz breccia is composed of clasts of country rock and carbonatite ranging from <1 mm to ~30 cm in size, cemented by ankeritic carbonatite. Extensive fenitisation and biotitisation mainly affects clasts of coarse-grained granitoids and medium-grained dolomite-calcite-carbonatites. An intersection of Storkwitz breccia at 425 m to 542 m contains local REE-enrichment up to ~1.7 wt.%. TREO, which is predominantly contained in a REE-fluorcarbonate bearing mineral assemblage. The assemblage locally forms irregular-shaped vug-like features and rare hexagonal pseudomorphs in clasts of fine-grained ankerite-carbonatite. The REE-fluorcarbonate mineral assemblage formed prior to brecciation in the ankerite-carbonatite, which paragenetically fits with recent experimental and fluid inclusion data demonstrating the importance of late magmatic processes in forming carbonatite-hosted REE mineralisation, possibly from an evolved 'brine-melt' phase. Our findings indicate that minor REE recrystallization and redistribution occurred during late-stage hydrothermal or supergene processes, without leading to significant REE enrichment in the upper part of the breccia compared to the lower part. Cross-cutting faults represent the last deformation event and post-date carbonatite intrusion and fenitisation. They may represent important conduits for late-stage hydrothermal or supergene fluids responsible for recrystallization of the breccia matrix to a cryptocrystalline oxide mineral assemblage. Our findings highlight the importance of REE enrichment in late-stage 'brine-melt' phases through magmatic fractionation and *in-situ* hydrothermal replacement.

Keywords: carbonatite, REE, 'brine-melt' phase, burbankite replacement, Storkwitz

Introduction

Historically, carbonatites have been classified using the descriptive approach as igneous rocks composed of more than 50 % carbonate minerals (Le Maitre *et al.* 2002). Significant advances in understanding carbonatite systems allow genetic classification of carbonatites as carbonate-rich cumulate igneous rocks formed in the crust by fractional crystallisation of carbonate-rich parental melts which are ultimately mantle-derived (Yaxley *et al.* 2022). Carbonatite-related mineralising systems represent outstanding multi-commodity exploration targets due to their extreme primary enrichment in the light rare earth elements (LREE), strontium, niobium, phosphorus, and fluorine, among others (Simandl and Paradis 2018; Anenburg *et al.* 2021). They are therefore among the principal economic sources for these commodities, especially the REE (Verplanck *et al.* 2016). For example, current REE production predominantly hails from the Bayan Obo, Daluxiang and Weishan mining districts in China, as well as from the Mount Weld mine, Australia, and Mountain Pass, USA, all of which are carbonatite-related deposits (Wall 2014; Barakos *et al.* 2016, Poletti *et al*. 2016, Watts *et al.* 2022). Recent decades are characterised by growing REE demand due to their use in high-strength permanent magnets and other high-tech industries (Goodenough *et al.* 2018), but the REE are also susceptible to future supply interruptions due to price and supply volatility (Paulick and Machacek 2017). Consequently, REE are classed as critical metals by the European Union (EU) as the EU is highly dependent on REE imports and, therefore, vulnerable to supply disruptions (European Commission 2020). In this context, re-assessment of domestic deposits in Europe, such as Fen (Norway), Norra Kärr (Sweden), and Storkwitz (Germany) is of considerable economic and research interest (Goodenough *et al*. 2016). Understanding the mineralogy of a deposit is important for its economic viability because out of >200 known REE-bearing minerals only bastnäsite, xenotime and monazite are currently processed for production (Charalampides *et al.* 2015). In this contribution we investigate the Storkwitz breccia, which is part of the larger late Cretaceous ultramafic lamprophyre-carbonatite Delitzsch complex.

Previous studies of the Delitzsch complex focussed on petrographic characterisation of carbonatites and lamprophyres to understand the timing of magmatism and the magmatic evolution of the complex itself. Investigations into the rare earth mineralisation hosted in the Delitzsch complex were not a major part of those studies. Recently, Niegisch *et al*. (2020) presented work on the 240–273 m interval of the SES 1/2012 drillore, obtained as part of an exploration program undertaken between 2011 and 2015 by Seltenerden Storkwitz AG (now

Ceritech), in order to understand REE mineralisation in the Storkwitz breccia. Our current work focuses on the 425–542 m intersection of the same SES 1/2012 drillcore, which was selected as hyperspectral imaging indicates high REE concentrations (Loidolt 2018; Müller *et al.* 2021). Here, we integrate our own observations with those of Niegisch et al. (2020) to understand REE mineralisation in the Storkwitz breccia in the wider context of carbonatite-related rare earth mineralisation. In particular, we characterise the alteration, REE mineralisation and mineralisation sequence of the carbonatites, and investigate the relationship between the REE mineralisation and the evolution of the complex.

Geology of the Delitzsch Ultramafic Lamprophyre – Carbonatite Complex

Regional Geology

The Delitzsch complex is located in northwestern Saxony, Germany, about 20 km north of the city of Leipzig (Krüger *et al.* 2013). It extends over an area of 450 km^2 and consists of lamprophyre and carbonatite intrusions and the associated Storkwitz and Serbitz breccia pipes (Krüger *et al.* 2013). The complex was intruded ~100–120 m below the pre-Cenozoic land surface and subsequently covered by ~100 m of Cenozoic glacio-fluvial sediments (Krüger *et al.* 2013; Niegisch *et al.* 2020). The basement is composed of Carboniferous to Lower Permian sediments underlain by Neoproterozoic to Cambrian sedimentary and volcano-sedimentary units of the Saxo-Thuringian zone to the south, and metamorphic rocks of the Mid-German Crystalline Zone to the North (Fig. 1; Röllig *et al.* 1990). The Delitzsch complex occurs at the intersection of the E-W trending Delitzsch–Doberlug synclinal zone and the N–S trending, seismically active Regensburg-Leipzig zone (Krüger *et al.* 2013), which Röllig *et al.* (1990) describe as a weakness zone separating two crustal blocks. The initial development of both structural zones is attributed to the Variscan orogeny, and these were later reactivated as extensional zones several times—namely during the development of the Oslo Rift, the opening of the Tethys and Atlantic Oceans, and lastly during the Alpine Orogeny (Marien, 2014). This most likely caused the development of horst and graben structures in the Delitzsch area (Wagner *et al.* 1997; Krüger *et al.* 2013). The structural intersection between the Delitzsch–Doberlug and Regensburg–Leipzig zones controlled melt ascent (Röllig *et al.* 1990). Shallower, younger NW–SE trending structures controlled melt emplacement and the location and shape of the breccia pipes, including Storkwitz (Röllig *et al.* 1990).

Geology of the Delitzsch Complex

Lamprophyres at the Delitzsch complex commonly form centimetre to metre thick, steeply dipping, homogeneous dykes which predominantly consist of alnöite (biotite and melitite dominated commonly with olivine, calcite, and clinopyroxene), with minor occurrences of monchiquite (olivine, clinopyroxene, and biotite or amphibole phenocrysts with a groundmass of glass or feldspathoids) and aillikite (carbonate-rich lamprophyre with olivine, diopside, amphiboles and phlogopite phenocrysts in a matrix with primary carbonate but no melilite) (Gruner 1990; Seifert *et al.* 2000; Krüger *et al.* 2013). The breccia pipes at Storkwitz and Serbitz contain abundant lithologically-variable clasts, including angular to subangular wall rock rhyolites and metasedimentary rocks, as well as rounded to sub-rounded carbonatite and ultramafic lamprophyre from deeper in the complex (Röllig *et al.* 1990; Krüger *et al.* 2013).

Carbonatites in the Delitzsch complex form steeply dipping, E–W trending dykes, veins and pipe-shaped bodies up to tens of metres in diameter (Röllig *et al.* 1990). Both dolomite-ankerite-carbonatites and fine-grained, porphyritic calcite-carbonatite veins contain accessory apatite, magnetite, sulfides and phlogopite (Röllig *et al.* 1990; Niegisch *et al.* 2020). Röllig *et al.* (1990) proposed a four-stage emplacement sequence based on crosscutting relationships of lamprophyres and carbonatites as well as variations in the xenolith content in carbonatite breccias, which was later modified (Krüger *et al.* 2013). Krüger *et al.* (2013) used U-Pb dating of zircon and baddeleyite from dolomite-carbonatite and Rb-Sr dating of phlogopite from ultramafic lamprophyres to constrain the main phase of emplacement to 75–71 Ma, comprising (in order of emplacement): (a) ultramafic and alkali lamprophyres, (b) carbonatitic breccia pipes with xenoliths of ultramafic lamprophyre and dolomite-carbonatite, (c) the intrusion of lamprophyre within the breccia pipes, (d) formation of xenolith-bearing dolomite-carbonatite dykes, (e) formation of xenolith-free dolomite-carbonatite dykes, and (f) late-stage calcite-carbonatite dykes, which locally contain xenoliths (Krüger *et al.* 2013). Thin reaction rims around xenoliths and the preservation of xenoliths in extreme disequilibrium with the melt may be the results of rapid emplacement and crystallisation (Krüger *et al.* 2013). The appearance of carbonatites, granitoid fenites and glimmerite clasts hosted in carbonatite breccias indicates the presence of a fenite aureole at depth (Röllig *et al.* 1990).

Magmatic History

A close genetic relationship between the lamprophyre and carbonatite at Delitzsch is indicated by their cross-cutting relationships (Röllig *et al.* 1990), and is supported by overlapping $^{87}Sr/^{86}Sr$ values for these rocks (carbonatite: 0.7036–0.7049, lamprophyre 0.70347±4; Krüger *et al.*, 2013) and the similar chemical compositions of accessory minerals such as phlogopite (Seifert *et al.* 2000; Krüger *et al.* 2013). Phlogopite compositions exhibit increasing Ti, Al, Cr, Ba and Na and decreasing Mg and F contents from early to late rocks at the complex, while apatite increases in S, Cl, Si and decreases in REE, Sr, Na, F (Seifert *et al.* 2000). Apatite-phlogopite geothermometry and hydrogen-fluoride barometry indicate that carbonatites formed from melts produced during several magmatic events. The emplacement sequence from dolomite-carbonatite to late-stage calcite-carbonatite dykes (stages b to f) cover temperatures from 1200°C to around 600°C (Seifert *et al.* 2000). The Delitzsch phlogopite has higher TiO_2 and Al_2O_3 concentrations and lower Cr_2O_3 concentrations compared to mantle xenolith mica and MARID-like rocks (Krüger *et al*. 2013). In combination with the $^{87}Sr/^{86}Sr$ ratios, the phlogopite compositions indicate that it is dominantly xenocrystic and derived from the same, lamprophyre-like sublithospheric mantle source.

FIG. 1. (a) Regional overview map of Germany with the location of the Delitzsch ultramafic complex. (b) Geological map of the Delitzsch area with Cenozoic cover removed, dashed grey line is the line of section presented in (c). (a) and (b) simplified after Krüger et al. (2013). (c) schematic cross section of the Storkwitz diatreme (modified after Möckel 2015). RHZ, Rheno-Hercynian zone; SX-TH, Saxo-Thuringian zone; UML, ultramafic lamprophyre.

Exploration History

The Delitzsch complex was investigated by drilling over 500 holes, reaching depths of 1100 m, during two exploration campaigns (Seifert *et al.* 2000). Initially, a uranium prospecting and exploration program was carried out by the SDAG Wismut in collaboration with the Central Geological Institute (ZGI) in Berlin around the known Permian intrusions of the Delitzsch–Halle area between the late 1960s and 1989 resulting in the discovery and verification of the rare earth resource hosted by the Storkwitz breccia (Möckel 2015). Carbonatite- and carbonatite breccia-hosted REE mineralisation has been intercepted in 143 drill holes over a 20 km² area, along with elevated concentrations of Nb, Ta, P and Th (Kormeier & Miroschnitschenko 1979). Renewed interest in the REE resource led to further drilling between 2011 and 2015 by Seltenerden Storkwitz AG (now Ceritech), delineating an estimated JORC compliant resource of 4.4 Mt, grading 0.45 wt.% total rare earth oxides (TREO) (Deutsche Rohstoff AG 2013). However, the Storkwitz breccia does not form an economically viable deposit because (a) no uniform carbonatite massif is known, (b) the ore bodies are too far apart, and (c) the complex is beneath thick Cenozoic cover which contains important groundwater aquifers (Kormeier & Miroschnitschenko 1979; Deutsche Rohstoff AG 2013).

Recent work carried out by Niegisch *et al.* (2020), focussed on the geochemical and mineralogical characterisation of the REE mineralisation of the upper zone (240–273 m) of the SES 1/2012 core. Niegisch *et al.* (2020) demonstrated that, in this part of the core, REE mineralisation is associated with a heterogeneous carbonatitic igneous breccia body and several fine-grained calcite-carbonatite veins. The principal REE ore minerals are secondary monazite and REE-fluorcarbonates occurring in both the igneous breccia and the fine-grained calcite-carbonatite veins (Niegisch *et al.* 2020). The authors interpret supergene overprinting as a key process responsible for the intensive alteration textures and parageneses of different minerals, the recrystallisation of the breccia matrix, the formation of supergene iron oxyhydroxides and the redistribution of REE to new REE mineral phases. In this contribution we investigate the deeper part of the core, below the area investigated by Niegisch *et al.* (2020), where the effect of supergene processes is expected to be much lower.

Methodology

A total of 26 samples (Table 1) were taken during core logging, encompassing country rock lithologies, carbonatite clasts, alteration zones and other regions of interest. On all samples, which were prepared as ~200 µm thick sections, optical microscopy was performed using a M2m (Zeiss) microscope, and mineral liberation analysis (MLA, automated EDS mineral identification system) using a FEI Quanta 650 MLA-FEG.

Optical microscopy and mineral liberation analysis (MLA) were used for mineral identification, textural analysis and establishing paragenetic relationships. Representing MLA data as mineral distribution maps was particularly helpful because of the fine-grained nature of the samples, which obscured many features in optical microscopy. Semi-quantitative REE concentrations from MLA data highlighted particularly REE-rich and REE-poor samples.

Following thick section preparation sufficient material for quantitative X-ray diffraction analysis (XRD) was left from 22 samples. XRD analysis provided quantitative mineralogical data which was used to improve the mineral list used for MLA. XRD texture specimen analysis was used to identify the clay minerals present based on their characteristic diffraction peaks.

Of those twenty-two samples, five samples, which are representative of the different carbonatite types classified based on mineralogy, were selected for X-ray fluorescence analysis (XRF) for geochemical classification of the carbonatite types present. Carbonatite was carefully extracted from individual clasts in these samples in order to avoid the problems of contamination inherent from 'whole rock' analysis of breccias, and preference was given to fine-grained carbonatites to reduce issues relating to inhomogeneity when sampling smaller volumes.

TABLE 1. SAMPLE TABLE WITH SAMPLE DEPTH; LITHOLOGY AND Ce-CONCENTRATIONS TAKEN FROM THE MLA CALCULATED ASSAY TABLE. SAMPLE LOCATIONS ARE SHOWN IN FIG. 2.

Sample Number	Depth (m)	Lithology	MLA Calculated Assay Ce (wt.%)
DE-CLO_01	425.5	Granitoid	

DE-CLO_02	427.9	Intrusive breccia with granitoid clast	
DE-CLO_03	428.7	Intrusive breccia with fenitised granitoid clast	
DE-CLO_04	429.2	Granitoid with fenite vein	
DE-CLO_X	429.3	Intrusive breccia, REE-fluorcarbonate blebs in ankerite-carbonatite clast	1.14
DE-CLO_05	429.4	Ankerite-carbonatite with REE-fluorcarbonates, biotite	4.77
DE-CLO_06	436.9	Intrusive breccia, faulted	
DE-CLO_07	443.6	Dolomite-carbonatite with apatite, biotite, partially oxidised sulfides	
DE-CLO_08	445.4	Granitoid, fenitisation overprints REE-fluorcarbonate-ankerite-carbonatite vein	
DE-CLO_09	453.4	Carbonatite with biotite glomerocryst	
DE-CLO_10	453.8	Granitoid, fenitised	
DE-CLO_11	456.35	Ankerite-carbonatite clast in matrix, REE-fluorcarbonate assemblage with beige and red blebs	7.11
DE-CLO_12	479.4	Granitoid, fenitisation overprints REE-fluorcarbonate – ankerite-carbonatite vein	
DE-CLO_13	489.5	Intrusive breccia, large pyrite and biotite fragments	
DE-CLO_14	493.7	Carbonatite with apatite & biotite, fenite vein	
DE-CLO_15	496.8	Carbonatite with siderite, pyrite & apatite, partial oxidation, fenitised; matrix contains fenitised granitoid clasts	
DE-CLO_16	498.7	Completely fenitised, unknown protolith	
DE-CLO_17	511.6	Intrusive breccia, fenitised granitoid fragment & pink porphyritic granitoid fragment	
DE-CLO_18	513.7	Intrusive breccia, REE-fluorcarbonate blebs in ankerite-carbonatite clast	2.17

DE-CLO_19	514.1	Intrusive breccia, partially oxidised sulphide & granitoid clasts	
DE-CLO_20	515.2	Intrusive breccia, fenitised granitoid clasts, sulphide fragment	
DE-CLO_21	518.7	Dolomite-carbonatite with pyrite, biotite & apatite	
DE-CLO_22	534.7	Intrusive breccia, REE-fluorcarbonate blebs in ankerite-carbonatite clast	3.08
DE-CLO_23	536.7	Intrusive breccia, granitoid clast	
DE-CLO_24	536.8	Granitoid, fenitised	
DE-CLO_25	536.95	Granitoid, fenitised	

Mineral Liberation Analysis

Mineral liberation analysis (MLA) is a software package developed to process SEM-EDS data (Gu 2003; Fandrich *et al.* 2007). Grain-based X-ray mapping (GXMAP), also known as Ford analysis (Fandrich *et al.* 2007), was employed during this study. High-resolution BSE images and GXMAP data were collected on a FEI Quanta 650 SEM using MLA Suite 3.1 software. The SEM-EDS was run with an accelerating voltage of 25 kV, a beam current of 10 nA and acquisition time of 7 ms per spot. The BSE detector was calibrated to the 253 grey-scale value of gold. The MLA spot size is 5.66 µm with a 500×500-pixel frame resolution, a 6×6-pixel step size, a horizontal field width of 1500 and a 25–255 grey-scale value BSE mapping trigger. Modal mineralogy, calculated assays, elemental distribution, and mineral associations were exported from the MLA software (Bachmann *et al.* 2017).

X-Ray Diffraction Analysis

Whole-rock samples of ~2.5 ml volume were wet-milled by use of a McCrone mill (Retsch, zirconium oxide grinding media, in ethanol). After de-agglomeration of the dried samples in a MM400 mixer mill, they were prepared into 27 mm sample holders using the back loading technique. Quantitative XRD phase identification was carried out using a PANalytical Empyrean X-ray diffractometer, which is equipped with a Co-tube (with primary Fe-filter) operated at 35 kV and 35 mA, and a PIXcel 3D medipix 1×1 area detector. Samples were measured in the 5–80° 2θ interval with a step size of 0.013° 2θ for a total measurement time of 153 minutes. The irradiated area was kept constant using an automatic divergence slit at 15×12 mm. Data was evaluated using the pdf4+ 2020 database (ICDD) and the Highscore Software package of pdf4+ PANalytical as well as the BGMN/Profex software package (Doebelin and Kleeberg 2015) based on Rietveld refinement. Raman spectroscopy identified the presence of dolomite, ankerite and kutnohorite, which cannot be identified by XRD alone due to peak overlaps.

In addition, three XRD oriented specimens (Brindely and Brown 1984) were prepared from two XRD whole-rock samples and a vug-like feature filled with an unknown clay mineral. After elutriation and homogenisation around 150 mg sample material was subjected to XRD oriented specimen analysis after drying room temperature. Vapour coating with ethylene glycol for 24 hours at 80°C preceded the second measurement, while heating the samples to 350°C and to 550°C for 2 hours each preceded the third and fourth XRD measurements, respectively. The XRD oriented specimens were analysed qualitatively in the 4–17° 2θ (22–6 Å) and 26–31° 2θ (4–3.34 Å) intervals for the diagnostic diffraction peaks for common clay minerals (Brindley and Brown 1984).

X-Ray Fluorescence Analysis

XRF analyses were undertaken on the same samples as prepared for XRD. The <63 µm material was dried at 105°C, weighed and roasted at 950°C for 2 hours to obtain the loss on ignition value (LOI). Sample material and lithium tetraborate [$Li_2B_4O_7$] were mixed in a 1:8 ratio and fused at max 1100°C for around 1 hour in a Claisse TheOX Advanced furnace. Fused vugs were measured with a wavelength dispersive PANalytical Axios^{MAX} XRF fitted with a Rh anode and using SuperQ 5 software. The wide-range oxides (WROXI) program was employed for quantified major element analysis. Measurements were recorded with 25–60 kV voltage and a 66–160 mA current based on elements analysed and measurement programmes used. Obtained oxide concentrations in wt.% were corrected for LOI using the formula of Willis *et al.* (2014).

Observations on the Composition and Texture of the Storkwitz Breccia

Seltenerden Storkwitz AG drilled SES 1/2012 in 2012 to intersect the entirety of the Storkwitz breccia. The hole is located at 51.53499° N, 12.28383° E, has an azimuth of 327° and a dip of 12.1°, and reaches a total length of 700 m (Ceritech 2012; Fig. 1C). The hole is composed of 138 m of Cenozoic glacio-fluvial cover before intersecting porphyritic granitoid wallrock from ~138 to 246 m. A lamprophyre intrudes the porphyritic granitoids at 182 to 188 m and a deeper calcite-carbonatite dyke intrudes at 242 to 244 m. Altered lamprophyres (246–252 m) overlie the Storkwitz breccia occurring between 252 and 640 m before the hole passes into a footwall of metamorphosed sedimentary rocks from 640 m, which includes silty mudstones with veins of intrusive carbonatite material (Ceritech 2012; Fig. 1C). The breccia is divided into an upper zone (252-269 m) and a lower zone (372–640 m), separated by a series of faulted and brecciated porphyritic granitoids and an extensive fault zone at 361–372 m. Further faults crosscut the breccia at ~417 m and ~556 m. Fine-grained calcite-carbonatite dykes intruded the breccia at ~381–385 m and ~615 m and a lamprophyre dyke intruded at 626–628 m. The upper part of the Storkwitz breccia contains porphyritic granite clasts up to several metres in diameter and is extensively cut by fine-grained calcite-carbonatite veins from 253–265 m (Ceritech 2012).

The interval analysed in this study (425–542 m) forms the central part of the lower zone of the Storkwitz breccia body (Fig. 2). This particular interval was selected as hyperspectral imaging spectroscopy (HSI) indicates high REE concentrations (Loidolt, 2018; Müller *et al.* 2021) and complements similar work undertaken at a higher level in the same drill core (240–273 m; Niegisch *et al.* 2020). The chosen core interval is a well-cemented breccia containing clasts of country rock sediments and granitoids. The proportions of different country rock types and angularity of clasts varies with depth and several breccia subtypes can thus be distinguished (Supplementary table 1). Coarse-grained granitoid clasts are abundant throughout the studied interval, whereas clasts of porphyritic granitoids and sedimentary rocks predominantly occur in two intervals (porphyritic granitoids: 437–444 m and 527–542 m; sedimentary rocks: 437–444 m and 532–544 m). A zone of very severe core loss and intense chloritisation between 435.80–437 m indicates a fault zone. Several fragments in this zone show striations (Fig. 3 C) but the sense of movement could not be identified because the core is not orientated.

FIG. 2. Downhole lithological logs from Ceritech (2012) and this study.

The observations below are the combination of findings of core logging, optical microscopy, MLA and XRD analysis with supplementary XRF analysis.

Breccia

The principal unit over the studied interval is a matrix-supported breccia composed of clasts of multiple lithologies, ranging in size from <1 mm to ~30 cm, cemented primarily by carbonate minerals, mainly ankerite (Supplementary Fig. 1 A). The clasts comprise coarse-grained granitoids, porphyritic granitoids, fine-grained dark sedimentary rocks, several carbonatite types and rare glimmerites. White reaction rims of a few mm to sub-mm thickness surrounding country rock clasts occur throughout the breccia (Fig. 3 A, B). The breccia matrix is beige-coloured, well cemented and primarily composed of ankerite and clays with minor Fe(-oxy)-hydroxides (Supplementary Fig. 1 A-F) and contains numerous micro-fragments of carbonatite and granitoids as well as sulfides, apatite and minor concentrations of REE-fluorcarbonates. Localised dark brown oxidised spots are associated with sulfide blebs and more diffuse brown matrix areas are associated with less localised oxidation.

FIG. 3. (a) White reaction rim around granitoid clast at 489–490 m. (b) White reaction rim around porphyritic granitoid clast at 511–512 m. (c) Striations on chloritized clasts in a fault zone crosscutting the carbonatite breccia at 435.80-437 m.

Country Rock Clasts

Granitoid fragments are coarse-grained and mainly composed of K-feldspar with less abundant quartz and plagioclase and variable contents of alkali-amphiboles, alkali-pyroxenes, and biotite (Supplementary Fig. 2 A, D-I). The clasts are variably altered. Relatively unaltered coarse-grained granitoids are pale in colour, while altered zones are finer grained, locally fibrous, and green to brown in colour due to the presence of ferromagnesian minerals (Supplementary Fig. 2 A, D-I).

Porphyritic granitoids are pale-coloured and consist of plagioclase and quartz phenocrysts in a very fine-grained K-feldspar groundmass (Supplementary Fig. 2 B). Localised alteration results in a colour change to intense pink, attributable to a substantial decrease in the abundance of plagioclase in these rocks.

Clasts of sedimentary rocks are dark grey to black, very fine-grained, subangular to angular fragments which are locally foliated (Supplementary Fig. 2 C). The main constituent is orthoclase with minor albite, quartz, biotite, and rare chlorite. The clasts show a low degree of alteration dominated by clay formation associated with thin quartz-pyrite veins and small disseminated pyrite grains.

Carbonatites

Based on whole-rock XRF data (Supplementary table 2), most carbonatite clasts in the breccia classify as magnesiocarbonatite, except for a single sample which extends into the ferroan calciocarbonatite field (Le Maitre 2002; Mitchell 2005; Fig. 4). Based on MLA data, ankerite is the most abundant carbonate mineral and constitutes the groundmass of most carbonatite clasts (Supplementary table 3). Dolomite and calcite are less abundant than ankerite. Based on their mineral assemblage (Supplementary table 3) and texture, they can be divided into three types:

1. Fine-grained dolomite-carbonatite clasts with minor ankerite (Supplementary Fig. 3 A-B). These contain various accessory minerals: abundant, partially oxidised, pyrite, marcasite, and sphalerite, as well as magnetite, biotite, apatite and pyrochlore. All accessory minerals appear to be primary and show signs of alteration—mainly oxidation and embayed margins. Apatite forms thin, wavy, discontinuous bands.

2. Medium-grained mixed ankerite-dolomite-calcite-carbonatites, which are characterised by the highest calcite contents (Supplementary Fig. 3 C-D). Abundant accessory minerals include REE-poor apatite and biotite, with minor pyrochlore and pyrite (Fig. 5). A fibrous richterite vein cuts across this sample (Supplementary Fig. 3 C, E). Biotite locally occurs as glomerocrysts (Supplementary Fig. 3 D), which can be partially altered to richterite.

3. Fine-grained ankerite-carbonatites, which are the most abundant. They are characterised by beige-coloured vug-like features, ranging in size from ~1 mm to ~6 cm, which predominantly contain bastnäsite with minor Ca-Mg-smectites, baryte, gypsum, celestine, quartz, amorphous silica, aegirine, alkali-amphiboles, chlorite, sulfides, and secondary iron oxides (Fig. 6 A-B, Supplementary Fig. 3 F-H). Red quartz-REE-fluorcarbonate vug-like features are rarer (Fig. 6 A-B, Supplementary Fig. 3 F-H), but show the highest REE concentrations.

FIG. 4. Carbonatite classification diagram after Le Maitre (2002). Sample numbers are located next to the dots. I - calcio-carbonatite. II - magnesio-carbonatite, III - ferro-carbonatite. Typical magmatic evolution of carbonatite magmas after Smithies & Marsh (1998), Simandl & Paradis (2018) and Anenburg et al. (2020).

REE and REE-bearing minerals in the Storkwitz breccia

The following descriptions are primarily based on MLA mineral maps and the corresponding BSE images. Virtually all REE in the Storkwitz breccia are concentrated in REE-fluorcarbonates, with subordinate monazite, hosted in fine-grained ankerite-carbonatite. Most niobium in the samples is contained in pyrochlore, with a minor amount of ilmenorutile.

Apatite and Pyrochlore. Apatite is an abundant accessory mineral in fine-grained dolomite-carbonatite (Fig. 5), medium-grained mixed ankerite-dolomite-calcite-carbonatite clasts and in the breccia matrix. It forms anhedral to subhedral crystals, which are locally embayed, have a spongy texture and exhibit well-defined concentric zoning (Fig. 5). The grains form either fan-shaped crystal clusters or discontinuous wavy bands aligned along their long axis (Fig. 5).

Pyrochlore mainly forms rare, large euhedral to subhedral crystals, which are embayed and often have a spongy texture (Fig. 5), in fine-grained dolomite-carbonatite and medium-grained mixed ankerite-dolomite-calcite-carbonatite clasts. Apatite and pyrochlore are minor accessories in fine-grained ankerite-carbonatite clasts.

FIG. 5. BSE images of (a) BSE image of an embayed pyrochlore crystal (bright) with a spongy texture surrounded by slightly embayed long-prismatic apatite crystals (medium grey) in carbonates (dark grey) (DE-CLO_14). (b) Pyrochlore crystal (bright) with a spongy texture and lightly zoned long-prismatic apatite crystals (light grey) with zoned biotite crystals (darker grey) (DE-CLO_14).

REE-fluorcarbonates. Zoned REE-fluorcarbonate crystals were identified as bastnäsite and synchysite by Niegisch *et al.* (2020). REE-fluorcarbonates form small (<50 µm) laths and plates, which predominantly form rose-shaped agglomerates (Fig. 6 C, D). Some crystals are concentrically zoned (Fig. 6 D). REE-fluorcarbonates principally occur in beige rounded vug-like features contained within ankerite-carbonatite clasts (Fig. 6 A, B) and ankerite veins cross-cutting altered coarse-grained granitoids (Supplementary Fig. 2 D, F). They can also form thin rims around rock and mineral fragments hosted within the ankerite-dominated breccia matrix (Fig. 6 E). The REE-fluorcarbonate mineral assemblage locally forms pseudomorphs after an unknown hexagonal, euhedral to subhedral mineral (Fig. 6 F). Minerals associated with REE-fluorcarbonates in these vug-like features include monazite, apatite, Mg-Ca-smectite, baryte, gypsum, celestine, quartz, amorphous silicate, aegirine, alkali-amphiboles, chlorite, sulfides and secondary iron oxides (Fig. 6 A, B). The proportions of these associated minerals vary widely. However, the very fine grain size and wide range of minerals associated with the REE-fluorcarbonate mineralisation makes the identification of these phases challenging.

Rare red-coloured REE-fluorcarbonate-bearing vug-like features also locally occur (Fig. 6 A, B). These are similar to the beige vug-like features described above but are dominated by quartz and REE-fluorcarbonates (Fig. 6 A, B). The beige and rarer red REE-fluorcarbonate assemblages also occur in the breccia matrix without obvious associated ankerite-carbonatite fragments.

FIG. 6. (a) MLA mineral map of beige (left) and red (right) REE-fluorcarbonate-bearing vug-like features in Mn-ankerite carbonatite clast (DE-CLO_11). (b) Photograph of DE-CLO_11 showing beige (left) and red (right) REE-fluorcarbonate-bearing vug-like features in Mn-ankerite carbonatite clast. (c) Detailed BSE image of REE-fluorcarbonate plates forming rose-shaped aggregates (DE-CLO_X). (d) Zoned REE-fluorcarbonate crystals (DE-CLO_05). (e) Thin REE-fluorcarbonate rim surrounding an aegirine-filled pseudomorph after an unknown mineral (DE-CLO_13). (f) Photomicrograph of the REE-fluorcarbonate

mineral assemblage (opaque material) forming pseudomorphs after euhedral – subhedral minerals (DE-CLO_05), shown in plane polarised light.

Monazite. Monazite is a minor phase and only occurs in fine-grained ankerite-carbonatites. It forms small, embayed crystals associated with REE-fluorcarbonates. Contact relationships between monazite and other minerals, especially apatite and REE-fluorcarbonates, are difficult to establish, which impedes the integration of monazite into the proposed mineralisation sequence.

Sulfides. Pyrite is the most abundant sulphide mineral, with marcasite and sphalerite as minor phases. Sulfides occur as: a) small, disseminated grains within the breccia matrix; b) partially oxidised crystals with frayed and embayed margins, and locally spongy texture, within carbonatite clasts; or c) macroscopic, broadly ellipsoidal and partially oxidised grains hosted in the breccia matrix. Sulfides are generally oxidised to varying degrees and surrounded by an iron oxide rim of variable thickness (Fig. 7 A, C). Large (>200 µm) pyrite crystals show complex intergrowth patterns, including banded and brecciated textures (Fig. 7 A). Very rare subhedral pyrite occurs throughout the samples and is nearly unaltered, homogeneous, and hosted in the matrix (Fig. 7 B). Rarely, pyrite also forms within thin quartz veins in the dark sedimentary country rocks (Supplementary Fig. 2 C).

FIG. 7. Reflected light photomicrographs of (a) Large altered pyrite with thick iron oxide rim hosted within a carbonatite clast (DE-CLO_20). (b) Rare cubic pyrite with embayed margin and small disseminated sulphide grains hosted within the matrix (DE-CLO_22). (c) Photograph of large, oxidised sulphide hosted within the breccia.

Aegirine, alkali-amphiboles and biotite alteration. Aegirine and the alkali-amphiboles mainly occur together (Fig. 8 A-C). Aegirine and amphibole-group minerals are the predominant ferromagnesian minerals in the granitoid clasts. These minerals also occur as fibrous veins in coarse-grained granitoid (Fig. 8 A, B) and carbonatite fragments (Fig. 8 D) as well as in completely altered clasts of an unknown protolith (Fig. 8 C). Aegirine and the alkali-amphiboles are often surrounded by concentrically zoned biotite (Supplementary Fig. 2 E, I). Rare fibrous or radial crystals of these minerals are hosted in fine-grained biotite crystal clusters.

Biotite occurs in the coarse-grained granitoid, porphyry and carbonatite clasts. It mainly occurs separately from aegirine and the alkali-amphiboles as a) euhedral to subhedral, often concentrically zoned crystals (Fig. 8 D); or b) as fine-grained crystal aggregates (Fig. 8 C). Aegirine and the alkali-amphiboles alter and replace biotite along the margin and along intra-crystal fractures (Fig. 8 C). Rare feathery biotite crystals are hosted in carbonatite fragments. Biotite rarely forms thin margins along ankerite-carbonatite veins (Fig. 8 B).

Areas of extensive biotite alteration often occur together with aegirine and the alkali-amphiboles. The alteration can be pervasive, completely altering some rock fragments (Fig. 8 C). Biotite and aegirine-alkali-amphibole alteration primarily affect coarse-grained granitoid clasts and is less extensive in medium-grained ankerite-dolomite-calcite-carbonatites and fine-grained dolomite-carbonatites, with minimal alteration in porphyritic granitoid clasts. Extremely rare, typically ellipsoidal mica agglomerates occur within the breccia matrix.

FIG. 8. (a) Alkali-amphibole-aegirine vein with Mn-ankerite cutting coarse-grained granitoid (DE-CLO_04). (b) Mn-ankerite carbonatite vein with REE-fluorcarbonate-bearing vugs with thin biotite rim cutting alkali-amphibole-aegirine altered granitoid (DE-CLO_12); note alkali-amphibole-aegirine altered areas cutting Mn-ankerite vein. (c) Completely biotite altered clasts cut by alkali-amphibole-aegirine veinlets (DE-CLO_16). (d) Alkali-amphibole-aegirine vein cutting dolomite-calcite-carbonatite with zoned euhedral-subhedral biotite (DE-CLO_14).

Discussion

Carbonatite mineralisation sequence

A mineralisation sequence including the carbonates, alteration minerals and REE-bearing minerals is shown in Fig. 9. Given that the mineralisation sequence is pieced together from breccia fragments, the evolution of the carbonatite complex, prior to brecciation, is unavoidably speculative. However, based on the range of carbonatite types, the predominance of ankerite, and the size of the complex, a multi-stage intrusive sequence is plausible - with a transition from calcio- via magnesio- to ferro-carbonatites, as is common in many carbonatite complexes (Le Bas 1987; Anenburg *et al*. 2020; Anenburg *et al*. 2021; Yaxley *et al.* 2022; Fig. 5 G). Manganese-bearing ankerite, rare kutnohorite and minor siderite evolved as late-stage carbonate phases. Common accessory minerals in dolomite-calcite-carbonatite and dolomite-carbonatite include apatite, biotite and sulfides, mainly pyrite. Other accessory minerals include pyrochlore and monazite. Several features of the dolomite-carbonatite fit with 'early' calcite- and dolomite-carbonatites from other complexes, such as rounded apatite grains (Chakhmouradian *et al.* 2017), biotite glomerocrysts and the presence of pyrochlore (e.g., Mitchell 2015; Giebel *et al.* 2017).

The REE-bearing dolomite-(ankerite)-carbonatite described by Kormeier & Miroschnitschenko (1979) corresponds to the REE-bearing ankerite-carbonatite identified in this study and probably represents a later stage component of the complex (Anenburg *et al.*, 2021). This unit is the principal host of REE mineralisation at Storkwitz although REE mineralisation has also been described in later fine-grained, porphyritic calcite-carbonatite dykes (Niegisch *et al.* 2020). Overall, the comparison of the results of hyperspectral analysis (Loidolt 2018) and mineralogical petrographic characterisation indicate the presence of three distinct REE-hosting mineral assemblages in the 425–542 m interval:

1) Minor amounts of REE are hosted in apatite, as well as biotite, pyrochlore and carbonates. However, identifying the nature of REE occurrences in these minerals was beyond the scope of this study. Most likely, REE are contained in µm-scale inclusions in biotite and carbonates, rather than in the crystal lattice.
2) A REE-fluorcarbonate mineral assemblage associated with vug-like features and hexagonal pseudomorphs in manganese-ankerite-carbonatite clasts and veins in coarse-grained granitoid clasts. This is the most common occurrence.
3) Rare REE-fluorcarbonate rims around clasts in the breccia matrix.

By comparing the order of emplacement and paragenetic sequence of the Storkwitz breccia with that of other carbonatite complexes, it is possible to infer that each of these stages reflects the progression from (1) magmatic conditions through (2) a (postulated) brine-melt fluid transitioning to (3) hydrothermal formation environments. These different stages are discussed below. Through comparison with the upper part of the SES 1/2012 drill core, we discount (4) supergene processes as having a major control on REE mineralisation at the Storkwitz complex.

1) *Early incorporation of REE in magmatic phases.* Early fractionation of apatite can remove significant REE amounts from a carbonatite melt and the presence of other rock-forming minerals with a limited capacity to accommodate REE, like phlogopite, amphiboles, calcite and dolomite, strongly affects apatite compositions (Chakmouradian *et al.* 2017). Significant variation in fluorine, strontium and REE concentrations in apatite were observed by Seifert *et al.* (2000) and minor REE concentrations in apatite, pyrochlore and carbonates were detected by Müller *et al.* (2021). However, experimental studies indicate that significant REE fractionation into apatite only occurs under two circumstances – a) very high silica activity, which suppresses dolomite and ankerite formation, or b) very late-stage alkaline conditions leading to high Na concentrations in apatite (Anenburg *et al.* 2020). Since abundant dolomite and ankerite formed in Storkwitz carbonatites and apatite is a significant early-forming phase in the calcite-and dolomite-bearing carbonatite clasts at Storkwitz, these circumstances are not applicable. Additionally, comparison of our MLA results with REE contents calculated from hyperspectral data and EDS data (Niegisch *et al.* 2020) indicate that apatite-rich samples are not particularly REE-rich and REE were enriched in the residual melt during mineral fractionation. Pyrochlore crystals are quite rare, fairly large and embayed with a spongy texture, indicating partial dissolution during later stages.
2) *Formation of REE minerals from a late magmatic 'brine-melt'.* REE mineralisation in carbonatites is commonly attributed to hydrothermal processes (e.g., Ngwenya 1994, Trofanenko *et al*. 2016, Broom-Fendley *et al*. 2016, 2017, Marien *et al*. 2018; Dietzel *et al*. 2019), where precipitation of REE-minerals is initiated by a change in temperature or pressure. While the prevalence of brecciation at Storkwitz clearly demonstrates that depressurisation and volatile release occurred at the complex, REE mineralisation and alteration predominantly occurs in the rocks prior to brecciation, primarily in manganese-ankerite-bearing carbonatite clasts within the breccia. Thus, the majority of REE

mineralisation occurs prior to depressurisation and REE mineral formation is related to other processes.

The predominance of REE mineralisation in later ankerite-bearing carbonatites at Storkwitz fits the notion that REE enrichment occurs through magmatic processes (Anenburg *et al.* 2020). As carbonatites evolve and fractionate REE-poor carbonate phases, the residual liquid is progressively depleted in Ca, Mg and Fe carbonate, and transitions from a carbonatite melt to a ‘brine-melt’ composition, rich in incompatible alkali and REE (Prokopyev *et al.* 2016; Anenburg *et al.* 2020). This residual liquid concentrates the REE and can lead to the precipitation of highly unstable alkali-REE-carbonate minerals, such as those of the burbankite and carbocernaite groups (Anenburg *et al.* 2020; Nikolenko *et al.* 2022). These can occur as euhedral crystals in carbonatite pegmatites (Zaitsev *et al.* 1998) and REE-rich veins (Tucker *et al.* 2012), as well as interstitial phases (Moore *et al.* 2015; Sitnikova et al., 2021), along grain boundaries (Platt and Woolley 1990) and preserved in mineral inclusions (Zaitsev and Chakhmouradian 2002; Chakhmouradian and Dahlgren, 2021). Owing to their solubility, preservation of burbankite and carbocernaite is rare and the most common manifestation of REE mineralisation in carbonatites is an assemblage of REE-(F)-carbonates with strontianite, baryte, and low-Sr calcite and/or quartz. Indeed, in many cases, evidence for the former presence of alkali REE-carbonates is limited to the occurrence of the above REE mineral assemblage in hexagonal pseudomorphs (Zaitsev *et al.* 1998; Andersen *et al.* 2017; Kozlov *et al.* 2020). Where REE-(F)-carbonates do not form as hexagonal pseudomorphs, they typically occur as vug-like features or vein-like habits. Such veins and vug-like occurrences may, however, represent areas of replaced anhedral alkali REE carbonates, as are preserved at the Khanneshin carbonatite complex, Afghanistan (Tucker et al., 2012).

Most REE mineralisation at Storkwitz forms as REE-fluorcarbonate-containing vug-like features in ankerite-bearing carbonatite which are beige-red in hand specimen (Fig. 5 A, B). Hyperspectral data and the magnetic susceptibility data of Niegisch *et al*. (2020) corroborate the existence of secondary iron minerals as the most-likely cause of the red appearance. The predominant iron phase is goethite in the beige matrix and REE-fluorcarbonate assemblages, whereas the rarer red zones have a higher magnetic susceptibility, potentially indicating hematite (Niegisch *et al.* 2020). The REE mineral assemblages do not typically exhibit a distinct shape. However, residual hexagonal crystal shapes occur in several samples (Fig. 6F) indicating a possible link to a hexagonal precursor mineral, possibly of the burbankite or carbocernaite groups. The REE-fluorcarbonate assemblage includes REE-fluorcarbonates, monazite, secondary sulphates, Mg-Ca-smectites, amorphous silica, quartz, sulfides, and secondary iron oxides (Fig. 6 A). This mineral assemblage is similar to REE-bearing mineral assemblages attributed to the destabilisation and breakdown of burbankite-group and other alkali-REE-carbonates (Anenburg *et al.* 2020; Kozlov *et al.* 2020; Anenburg *et al.* 2021). We therefore, on the basis of comparison with observations from other deposits and experimental data, tentatively attribute the formation of the REE minerals in the ankerite-bearing carbonatite to a ‘brine-melt’ formation process.

3) *Hydrothermal REE mineralisation.* Although most REE mineralisation occurs in manganese-ankerite-bearing carbonatite clasts, some REE mineralisation does also occur in the matrix of the carbonatite breccia. For example, Müller *et al.* (2021) and Niegisch *et al.* (2020) observed REE-fluorcarbonates and monazite forming thin rims around clasts as well as in areas of elevated porosity and along micro-fractures in the breccia matrix. In contrast to the REE-fluorcarbonate-dominated mineralisation in the 425–542 m interval of the Storkwitz carbonatite breccia, Niegisch *et al.* (2020) report monazite as the dominant rare earth ore mineral with lesser, but significant, REE-fluorcarbonate mineralisation. Our findings also support this observation, and we note the occurrence of (a) REE-fluorcarbonate rings around clasts in the breccia matrix (Fig. 6E), and (b) REE-fluorcarbonate-hosting cavities in quartz (Fig. 6A, B). Together, these features present evidence for minor syn- and / or post-brecciation REE transport, which locally redistributed REE, and is most-likely to be the result of a hydrothermal fluid. However, this transport is minimal and occurred primarily on the scale of millimetres to centimetres.

4) *Supergene Processes and REE mineralisation.* Niegisch *et al.* (2020) describe the complete breakdown of a carbonatitic breccia matrix and recrystallisation to a cryptocrystalline oxide mineral assemblage in the upper zone (240-273 m). In the groundmass of the breccia between 425–542 m, Fe-(Mg-Mn)-rich carbonate minerals are locally partially broken down, resulting in the exsolution of Fe-(Mg-Mn)-oxides and the recrystallisation to Fe-(Mg-Mn)-poorer carbonates. This breakdown is coincident with the formation of small iron oxide grains embedded in carbonate minerals and the local breakdown of sulphide minerals (Fig. 7A-C). Niegisch *et al.* (2020) attribute this extensive oxidation to supergene processes as the result of deeply percolating meteoric waters. While similar recrystallisation of matrix carbonates is observed in the lower zone, it has a minor effect and indicates a decreasing influence of supergene processes with increasing depth. Furthermore, Niegisch *et al.* (2020) compared REE content and LREE/HREE ratios between the oxidised upper part (240–273 m) and lower part (372–640 m) of the carbonatite breccia, based on their own and previous (Ceritech, 2012) geochemical data, which revealed similar LREE/HREE ratios and REE concentrations in the upper and lower part. This indicates that supergene processes did not lead to a significant REE enrichment in the upper zone (Niegisch *et al.*, 2020). While Niegisch *et al.* (2020) suggest that late-stage hydrothermal or supergene processes caused the recrystallisation of primary REE minerals to secondary monazite and REE-fluorcarbonates, we attribute this recrystallisation to the latest stages in the 'brine-melt' phase of the magmatic carbonatite evolution.

FIG. 9. Paragenetic sequence diagram for the Storkwitz breccia based on optical microscopy and automated mineralogical analysis.

Evidence for multiple carbonatite generations at depth

Owing to the thick cover of Cenozoic glacio-fluvial sediments, the structure and composition of the complex is not well known. Even in the deepest drill holes, the only units intercepted are country rocks, breccia pipes, and minor carbonatite and lamprophyre sills and dykes (Röllig *et al.* 1990). Most lamprophyres and carbonatites occur as breccias indicating rapid, partly explosive emplacement (Krüger *et al.* 2013). The close genetic relationship between lamprophyres and carbonatites indicates that they are derived from the same parental melt (Krüger *et al.* 2013). Based on the presence of calcite- and dolomite-carbonatite clasts, Röllig *et al.* (1990) proposed the existence of a dolomite-carbonatite intrusion with an associated fenite aureole at depth and multiple stages during the formation of carbonatitic breccias. Seifert *et al*. (2000) also suggest the formation of multiple dolomite-carbonatites, based on the range of composition of zoned phlogopite crystals.

Our findings from the SES 1/2012 drillhole corroborate the inferred presence of deep plutonic carbonatites and we similarly infer the presence of a multi-phase carbonatite pluton. The existence of multiple carbonatite bodies is indicated by:

a) Multi-stage fenitisation and biotitisation in coarse-grained granitic fragments and

b) Textural and compositional variation in carbonatite fragments in the breccia.

Multiple generations of aegirine and phlogopite occur in fenitised rocks at Storkwitz (Röllig *et al.* 1990). From our observations of the SES 1/2012 drillhole, we support the idea that fenitisation and biotitisation at Storkwitz occurred in multiple stages, and suggest two different discrete fenitisation events:

1) A first generation of aegirine, richterite and Na-Ca-amphibole, associated with an early carbonatite magma pulse crystallising dolomite-calcite-carbonatites and dolomite-carbonatites. Extensive biotitisation may predate or be largely synchronous with the later fenitisation event. Many biotite crystals are concentrically zoned, which indicates an evolution from iron-poor to more iron-rich biotite. The biotite surrounds or partially replaces aegirine and the alkali-amphiboles (Supplementary Fig. 2E, I).

2) A second fenitisation event associated with the later ankerite-carbonatite intrusion crystallised the second generation of aegirine and alkali-amphiboles, and partially altered biotite, mainly in the coarse-grained granitoids and earlier carbonatites (Supplementary Fig. 3D). Carbonate veins hosting the REE-fluorcarbonate mineral assemblage in coarse-grained granitoids are cross-cut by the fenite mineral assemblage (Fig. 8 B). This indicates

that the carbonate veins in coarse-grained granitoids predate either both or only the second fenitisation event.

Mineralisation of minor chlorite partially altering biotite occurred either synchronous with or after the second fenitization event.

Relationship between faults and REE mineralisation

Several fault zones were intercepted in SES1/2012 core, including the intensely chloritized fault zone at 435.8–437 m, which contains fragments showing striations. However, the sense of movement could not be identified because the core is not orientated. This fault zone cross-cuts the Storkwitz breccia most likely represents the last deformation event to affect this area (Fig. 10). Other fault zones intercepted in SES1/2012 core are also described as cross-cutting every lithology (Ceritech, 2012; Fig. 2). These fault zones could be important pathways for ascending low-temperature hydrothermal and/or descending meteoric fluids, and facilitate late-stage chloritisation of fenitised wallrocks and minor local REE redistribution into the breccia matrix. However, the effect of late-stage hydrothermal and/or supergene processes on rare earth mineralisation is minimal in the studied interval of 425–542 m. Mineralogic-petrographic characterisation of the studied interval suggests that evidence for fenitisation is restricted to plutonic carbonatite clasts and clasts of deep, primarily granitoid wall rocks. No alteration features corresponding to fenitisation are described from wallrocks intersected while drilling through the Storkwitz breccia (see Ceritech, 2012). Therefore, it is unlikely that these late, cross-cutting faults are related to fenitisation at depth.

In conclusion, the faults cross-cutting the Storkwitz carbonatite breccia are unrelated to primary magmatic-hydrothermal REE mineralisation and fenitisation of plutonic carbonatites and surrounding granitoid wallrocks.

FIG. 10. Schematic diagram summarising the evolution of the carbonatite intrusions, Storkwitz carbonatite breccia and REE mineralisation.

Conclusions

The Storkwitz carbonatite breccia hosts a variety of different clasts with sizes ranging from <1 mm to ~30 cm, cemented by a predominantly ankeritic matrix. The clasts represent country rock lithologies, mixed medium-grained ankerite-dolomite-calcite-carbonatites, fine-grained dolomite-carbonatites and fine-grained ankerite-carbonatites with associated REE mineralisation. REE mineralisation occurs in three stages:

1. Minor primary incorporation of REE into magmatic phases such as apatite.
2. A REE-fluorcarbonate mineral assemblage within the fine-grained ankerite-carbonatites and
3. Minor later REE mineralisation and redistribution in the matrix of the carbonatite breccia.

Based on the cross-cutting relationships, a multi-stage intrusive and mineralisation sequence is proposed:

1. The intrusion of an early carbonatite magma at depth crystallised a mixed medium-grained ankerite-dolomite-calcite-carbonatite and fine-grained dolomite-carbonatite with apatite, biotite, and sulfides as common accessory minerals. An associated fenitisation event primarily affected the coarse-grained granitoids.
2. An intrusion of fine-grained ankerite-carbonatites at shallower depth, which evolved to form widespread ankerite, Mn-bearing ankerite, late rare kutnohorite, and minor siderite. An associated fenitisation event mainly affected the coarse-grained granitoids and older carbonatites.
3. REE mineralisation in the fine-grained ankerite-carbonatites as a product of late-stage REE-enrichment of a residual ‘brine melt’, and breakdown of highly unstable alkali-REE-carbonates forming the current REE-fluorcarbonate mineral assemblage.
4. Explosive brecciation of the complex. Minor REE mineralisation by a hot, evolving hydrothermal fluid during a syn- or post-brecciation hydrothermal event forming REE-fluorcarbonate rings around clasts in the breccia matrix.

5. Supergene alteration of Fe-(Mg-Mn)-rich carbonate minerals in the breccia matrix, occurring more substantially in the upper part of the core than the lower part.

As this study indicates, the rare earth mineralisation hosted in the Storkwitz breccia is the result of the concentration of REE and other incompatible elements via primary magmatic fractionation prior to depressurization, and the REE were not introduced from an external source. The mechanism of this residual enrichment fits with the model of a 'brine-melt' liquid, as recently proposed (Prokopyev *et al.* 2016; Anenburg *et al.* 2020). Hydrothermal and supergene processes did not significantly further enrich the REE, but caused local REE redistribution.

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Appendix

SUPPLEMENTARY TABLE 1. DETAILED CORE LOG OF THE 425 – 542 m INTERVAL OF THE STORKWITZ BRECCIA.

From [m]	To [m]	Lithology	Sample ID	Description
425	426	carbonatitic breccia		Angular clasts, granitic rock at 425.31-425.50 m, some lapilli clasts within top ~3 core sections, thin white rims
426	427		1	Angular clasts, granitic rock at 426.32-426.59 m & 426.85-426.97 m, thin white rims decreasing in thickness towards 433 m
427	428		2	Substantial core loss at 427-427.60 m, angular clasts
428	429		3	Angular clasts, including dolomitic (carbonatite) clasts
429	430		X, 5	Angular clasts
430	431			Much core loss, granitic clasts at ~430-430.20 m and ~430.70-431 m
431	432			Severe loss between 431.30-431.56 m, pinkish-red granitic rock at 431.66-431.83 m
432	433			Severe core loss at 432-432.51 m, angular-subangular clasts
433	434			Angular clasts, core loss at 433.36-433,68 m, granitic rock at 433.80-434 m
434	435			Subangular-angular clasts, granitic rock with hematite veins at 434.18-434.95 m
435	436			Severe core loss, some chloritized clasts with striations at ~435.80-436 m
436	437		6	Extremely severe core loss

437	444		7	Much smaller, subangular clasts, 2 granitoid clast types (fine-grained from before + new, coarse-grained), fine-grained granitic clasts rare, coarse-grained granitic clasts dominant granitic clasts, more Cambrian clasts
444	451		8	More angular clasts, some subangular clasts
451	465		9, 10, 11	Both angular & subangular clasts, clasts get more subangular towards 465 m
465	482		12	Subangular clasts, become more rounded towards 482 m, thickness of white rims increases down to 489 m
482	498		13, 14, 15	Rounded clasts, become subangular towards 498 m, thickness of white rims increases down to 489 m & decreases down from 490 m
498	510		16	Subangular-angular clasts, become more angular towards 510 m, white rims decrease in thickness from 503-507 m
510	513		17	Angular-subangular clasts, some rounded clasts, very thin white rims (< 1mm) between 511-512 m
513	518		18, 19, 20	Dominantly rounded clasts, some subangular clasts, very thin white rims just before 514 m
518	532		21	Angular, subangular and rounded clasts, fine-grained granitic clasts reappear as more dominant at ~527 m
532	542		22, 23, 24, 25	Mostly angular clasts, some subangular, very big Cambrian clasts at 540-542, clasts size increases towards 542 m, missing core section at 537-539 m

SUPPLEMENTARY TABLE 2. WHOLE-ROCK XRF DATA OF REPRESENTATIVE SAMPLES OBTAINED FOR CARBONATITE CLASSIFICATION.

RESULTS ARE IN wt.%. NiO, CuO, PbO and HfO2 DATA BELOW THE DETECTION LIMIT OF 0.01 wt.%.

	LOI	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Mn_3O	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	V_2O_5	Cr_2O_3	SrO	ZrO_2	BaO	ZnO	Total

						4													
DE-CLO_5	36.48	3.76	0.052	0.84	9.54	4.68	11.72	24.38	<0.2	0.44	0.15	0.69	<0.01	0.041	1.89	<0.01	1.39	0.07	96.13
DE-CLO_9	26.39	20.50	0.228	4.30	6.9	1.26	8.59	23.39	1.25	1.31	2.05	1.01	0.03	<0.01	0.54	0.03	0.47	0.06	98.32
DE-CLO_14	29.31	9.190	0.081	1.64	3.39	1.11	7.97	35.71	0.42	0.26	6.43	0.43	<0.01	<0.01	1.37	0.03	0.28	0.02	97.63
DE-CLO_15	21.78	27.05	0.282	5.65	7.45	1.15	7.56	20.34	1.79	2.20	1.78	0.87	0.03	<0.01	0.39	0.04	0.44	0.06	98.87
DE-CLO_23	24.64	24.89	0.206	5.41	6.41	1.08	7.25	21.09	1.43	1.74	1.92	1.07	0.02	<0.01	0.48	0.03	0.58	0.05	98.30

Supplementary Figure 1. MLA mineral maps of breccia-dominated samples: (a) Manganese-bearing ankerite breccia matrix with carbonatite and country rock fragments (DE-CLO-06). (b) Manganese-bearing ankerite breccia matrix with fenitised granitoid fragments and clay-dominated vugs (DE-CLO-13). (c) Manganese-bearing ankerite breccia matrix with fenitised granitoid fragments and Mn-ankerite carbonatite clast with REE-fluorcarbonate filled vugs (top right) (DE-CLO-X). (d) Manganese-bearing ankerite breccia matrix with fenitised granitoid fragments and oxidised sulfides (top) (DE-CLO-03). (e) Mn-ankerite-brearing breccia matrix with pale-coloured coarse-grained granitoid fragments (DE-CLO-02). (f) Fenitised granitoid fragments and partially oxidised pyrite in Mn-ankerite breccia matrix (DE-CLO-20).

Supplementary Figure 2. MLA mineral maps of country rock samples: (a) Pale-coloured porphyritic granitoid (DE-CLO_01). (b) Pink porphyritic granitoid (right) and fenitised coarse-grained granitoid (left) (DE-CLO_17). (c) Foliated dark grey sedimentary rock fragment (DE-CLO_23). (d) Fenitised coarse-grained granitoid with REE-fluorcarbonate-ankerite vein with thin biotite rim (DE-CLO_08). (e) Fenitised granitoid with zoned biotite rims around richterite (DE-CLO-24). (f) Fenitised coarse-grained granitoid with REE-fluorcarbonate-ankerite vein with thin biotite rim (DE-CLO_12). (g) Fenitised coarse-grained granitoid (DE-CLO-25). (h) Coarse-grained granitoid with ankerite-fenite veinlet (DE-CLO-04). (i) Variably fenitised coarse-grained granitoids (DE-CLO-10). (j) Completely fenitised country rock (DE-CLO-16).

Supplementary Figure 3. MLA mineral maps of carbonatite fragments: (a) (a, b) Thick section images and MLA mineral maps of representative samples of the different carbonatite types: fine-grained ankerite-carbonatites (DE-CLO_05, DE-CLO_11). (c, d) fine-grained dolomite-carbonatites (DE-CLO_07, DE-CLO_21). (e, f) medium-grained dolomite-calcite-carbonatites (DE-CLO_09, DE-CLO_14). (g)

Supplementary Figure 4. *Photographs of the thick sections of each sample. Each thick section is around 2.6 cm wide.*