

The hydrothermal alteration of carbonatite in the Fen Complex, Norway: mineralogy, geochemistry, and implications for rare-earth element resource formation

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ABSTRACT

The Fen Complex in Norway consists of a ~583 Ma composite carbonatite-ijolite-pyroxenite diatreme intrusion. Locally, high grades (up to 1.6 wt.% total REE) of rare-earth elements (REE) are found in a hydrothermally altered, hematite-rich carbonatite known as rødbergite. The progressive transformation of primary igneous carbonatite to rødbergite was studied here using scanning electron microscopy and inductively coupled plasma-mass spectrometry trace-element analysis of 23 bulk samples taken along a key geological transect. A primary mineral assemblage of calcite, dolomite, apatite, pyrite, magnetite and columbite with accessory quartz, baryte, pyrochlore, fluorite and REE fluorocarbonates was found to have transformed progressively into a secondary assemblage of dolomite, Fe-dolomite, baryte, Ba-bearing phlogopite, hematite with accessory apatite, calcite, monazite-(Ce) and quartz. Textural evidence is presented for REE fluorocarbonates and apatite breaking down in igneous carbonatite, and monazite-(Ce) precipitating in rødbergite. The importance of micro-veins, interpreted as feeder fractures, containing secondary monazite and allanite, is highlighted. Textural evidence for included relics of primary apatite-rich carbonatite are also presented. These acted as a trap for monazite-(Ce) precipitation, a mechanism predicted by physical-chemical experiments. The transformation of carbonatite to rødbergite is accompanied by a 10-fold increase in REE concentrations. The highest light REE (LREE) concentrations are found in transitional vein-rich rødbergite, whereas the highest heavy REE (HREE) and Th concentrations are found within the rødbergites, suggesting partial decoupling of LREE and HREE due to the lower stability of HREE complexes in the aqueous hydrothermal fluid. The hydrothermal fluid involved in the formation of rødbergite was oxidizing and had probably interacted with country-rock gneisses. An ore deposit model for the REE-rich rødbergites is presented here which will better inform exploration strategies in the complex, and has implications for carbonatite-hosted REE resources around the world.

KEYWORDS: rødbergite, ICP-MS, SEM, carbonatite-ijolite-pyroxenite complex, REE mobility, monazite-(Ce), apatite, thorium.

Introduction

THE Fen Complex in southeastern Norway (Fig. 1) is one of the world's classic carbonatite complexes; it was here that the igneous nature of carbonatite was first recognized (Brøgger, 1921) and significant advances in the understanding of the petrology

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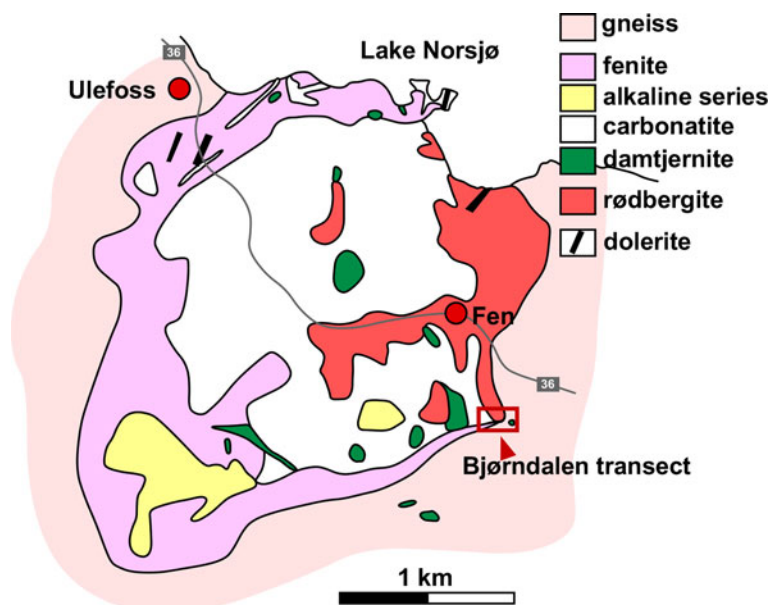


FIG. 1. Simplified geological map of the Fen Complex showing the main rock types and location of the sampling site (Bjørndalen transect) (after Sæther, 1957).

of carbonatites (Brøgger, 1921; Sæther, 1957; Ramberg, 1973; Griffin and Taylor, 1975; Mitchell and Brunfelt, 1975) and their *REE* contents (Andersen, 1984) were based on studies in the Fen Complex. The intrusion age of the Fen Complex is latest Neoproterozoic (583 ± 15 Ma by $^{40}\text{Ar}/^{39}\text{Ar}$ on phlogopite from a co-genetic ultramafic lamprophyre; (Meert *et al.*, 1998)). The plug-shaped Fen complex has an exposed surface area of ~ 6 km² (Fig. 1) and consists of a carbonatite-ijolite-pyroxenite composite intrusion (Bergstøl and Svinndal, 1960).

Carbonatites, igneous rocks with >50% carbonate minerals, show economic potential as they have the highest average concentration of *REE* of all magmatic rocks and considerable amounts of Nb and P (Cullers and Graf, 1984). *REE* are a resource of critical and strategic importance for present and future technology (European Commission, 2014). Carbonatite complexes such as Bayan Obo (China), Araxá and Catalão (Brazil) and Phalaborwa (South Africa) are the main sources for light rare-earth elements (*LREE*) and Nb, and also contain significant reserves of Cu, Ti, baryte, fluorite, vermiculite, Sr, V, Th, U and P (Mariano, 1989; Groves and Vielreicher, 2001; Cordeiro *et al.*, 2011; Smith *et al.*, 2015). The carbonatites of the Fen Complex contain a range of *REE* minerals, e.g. *REE* fluorocarbonates, monazite-(Ce), allanite, as well

as *REE*-bearing minerals such as apatite (Andersen, 1986). The highest *REE* concentrations (up to 15,000 ppm total *REE*) in the Fen Complex were detected in rødbergite (Mitchell and Brunfelt, 1975). Rødbergite ('red rock' in Norwegian) is usually defined as a calcite-dolomite carbonatite stained red by disseminated fine crystals of hematite (Andersen, 1984).

According to Andersen (1984, 1986, 1987a, 1987b) rødbergite formed by the replacement and alteration of ferrocarbonatites along zones of intense fracturing by hydrothermal fluids. The decrease in $\delta^{18}\text{O}$ and the increase in $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values indicate the influx of an oxidizing groundwater derived from a reservoir rich in radiogenic Sr (Andersen, 1984, 1986, 1987a, 1987b). The oxygen fugacity during the alteration increased subsequently and caused the oxidation of pyrite and the release of H^+ during the breakdown of pyrite supporting the dissolution of carbonate minerals. Andersen (1984, 1986, 1987a, 1987b) inferred a volume reduction of as much as 70 vol.% of rock for the most altered parts, which led to a residual enrichment of insoluble phases e.g. hematite and *REE* minerals. While *REE* minerals are considered to have been stable during the alteration, *LREE* were leached preferentially by the F-rich fluids; *MREE*, Y and Th are the least soluble elements in the

ferrocarbonatite and were strongly enriched in the solid residue (rødbergite) in this model.

Although Andersen's model for the formation of rødbergite is widely accepted in the scientific community, and has, for instance, recently been applied to the formation of similar rocks in the Gifford Creek Ferrocarbonatite Complex in Western Australia (Pirajno *et al.*, 2014), there are still open questions regarding the *REE* distribution and *REE* concentration mechanism within the Fen complex. *REE* exploration activities conducted by Fen Minerals AS and *REE* Minerals AS in recent years have produced new geochemical data and re-evaluated older data sets. These recent activities confirm rødbergite as the rock type with the highest average concentration of total *REE* (*TREE*) within the Fen Complex (21st North, 2014; Marien *et al.*, 2016). However, chemical data acquired by the Norwegian Geological Survey (1967–1970) shows a significant variation in *REE* concentration and variation in *LREE* to *HREE* ratios for rødbergite (21st North, 2014). *REE* are generally divided into two subgroups: the *LREE* (La to Sm) and *HREE* (Gd to Lu including Y) (Henderson, 1996). The present study reports new bulk-rock *REE* concentrations and mineralogical observations, and focuses on the detail of *REE* distribution and the *REE* concentration mechanism in the rødbergite. In order to learn more about the formation process of rødbergite, a coherent alteration transect from primary carbonatite to rødbergite has been sampled in detail for the first time and interpreted in terms of mineralogy, texture and geochemistry.

Methods

Based on fieldwork, several well exposed transitions from igneous carbonatite to rødbergite have been identified in the Fen Complex. In the present contribution, the focus is on the Bjørndalen transect in the eastern part of the Fen Complex (Fig. 1, UTM 32V 517541 6569595), as it provides an excellent insight into the transformation of carbonatite to rødbergite over a relatively short distance, which made it suitable for dense sampling. A series of 23 rock samples were taken along the ~30 m long Bjørndalen transect in order to represent the different stages of alteration from primary igneous carbonatite to rødbergite.

Mineral identification and textural analysis of samples was carried out by means of scanning electron microscopy (SEM) at the Plymouth Electron Microscopy Centre using a JEOL 7001 Field Emission Gun SEM equipped with a fast

Oxford Instruments EDS system for point analysis and for acquisition of large-area mosaics of high-resolution elemental maps (typically of several hundreds of fields), using an acceleration voltage of 15–20 kV and a working distance of 10 mm. Acquisition and data processing was carried out using Oxford Instruments' *Aztec* software.

Rare-earth element concentrations, as well as those of selected other elements (Nb, Th, U, Ta, Zr, Hf), were measured in solutions using the VG PQA3 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) in the trace-metal laboratory at Plymouth University. Initial digestions of rock powder by conventional multi-acid (HNO₃, HCl, HF) methods in Teflon vials at 220°C left insoluble material in the vast majority of the samples. Therefore, solutions were obtained by sodium peroxide sintering digestion according to Bokhari and Meisel (2016): 100 mg of sample was mixed with ~600 mg of Na₂O₂ (finely ground Merck analytical-grade granular sodium peroxide) in high-purity nickel crucibles and heated for 60 min at 480°C in a conventional muffle oven. The resulting sinter cake was dissolved in 90°C ultrapure water (Elga Purelab flex, >18.2 MΩ cm), centrifuged, and the clear solution decanted. The water-insoluble residue was dissolved in 3 mL of concentrated HNO₃ (analytical grade), and 1–5 mL of concentrated HCl (trace-element analysis grade) was added to dissolve any remaining iron oxides and hydroxides if present. After this step, no residue was left in any of the samples. The clear solutions were added together and made up to 100 mL in volumetric flasks using ultrapure water; effective dilutions were ~1000 times. Total procedural blanks, acid blanks and digestions of *REE*-1 Certified Reference Material (Strange Lake *REE*-Nb ore, Natural Resources Canada) were part of the analytical programme. Internal In-Ir standard solutions were added to each sample before ICP-MS analysis to correct for instrumental drift, and concentrations were calibrated with matrix-matched standard solutions spanning the full range of expected concentrations for each element (0.1–5000 ppb). Total procedural blanks were 0.5 ppb for Ce but <0.2 ppb for the other *REE*, typically 0.025–0.002 ppb for Eu–Lu. The relative precision and error (with respect to certified values) of the *REE*, Nb, Ta, Th and U concentrations, estimated by repeated analysis of the *REE*-1 CRM, were typically <4% and <15%, respectively. An empirical relation was used to correct for the interferences of CeO and PrO on ¹⁵⁷Gd and of NdO on ¹⁵⁹Tb and on ¹⁶³Dy. These interferences were constrained by

TABLE 1. Trace-element concentrations (ppm) West to East along the transect.

	Carbonatite					Transitional carbonatite W					Rødbergite					Transitional Rødbergite E					Rødbergite				
	15-82	15-83	15-84	16-21	15-85	16-18	16-20	16-20/2	16-19	16-17	15-86	16-104	15-88	15-88/2	16-23	16-22	15-89	15-90	15-91	15-92	16-110	15-93	16-111	16-112	15-94
Y	53.6	62.9	50.6	57.1	50.2	76.0	133	128.9	47.2	51.8	214	96.3	270	232	292	214	110	80.6	126	101	108	191	319	144	288
Zr	281	898.7	71.2	34.4	52.9	37.0	66.2	76.5	52.5	58.6	588.3	96.4	252.7	338.7	167.1	148.5	153.9	214.9	229.6	234.8	135.9	381.8	294.3	208.5	737.2
Nb	580	989	220	355	84.4	100	47.3	39.7	<dl	<dl	166	331	167	1876	522	696	135	510	156	113	235	108	110	155	1020
La	313	297	136	284	120	353	113	130	109	149	444	292	502	455	108	1468	1326	2368	3344	2164	2348	3694	3712	2212	2705
Ce	667	677	355	431	426	733	426	417	406	367	876	453	1308	1234	336	2828	2678	4170	6117	4056	2715	6698	6890	4033	5212
Pr	60.6	58.9	33.8	51.0	40.7	68.4	41	40	36	39	82	58	179	161	39	316	295	440	651	435	474	706	732	446	550
Nd	223	220	131	186	148	253	160	155	130	134	323	229	676	602	189	1011	886	1307	2270	1298	1308	2414	2011	1275	1876
Sm	35.0	38.1	27.6	27.6	22.2	38.3	32.0	31.1	19.7	20.1	69.3	42.1	155.5	137.3	61.5	125.8	111.4	131.2	204.6	131.9	154.8	211.2	260.0	144.2	187.2
Eu	10.8	11.4	8.39	9.20	6.86	13.2	12.8	12.4	6.35	6.43	27.8	14.5	46.4	41.2	24.4	29.2	26.4	27.7	45.0	30.0	35.6	45.6	47.9	32.0	46.7
Gd	27.1	27.8	18.9	21.5	18.3	30.0	32.3	31.8	16.2	16.2	63.4	34.4	99.3	87.9	59.0	67.2	52.9	57.8	88.8	58.2	61.5	93.6	94.7	70.1	107.0
Tb	3.52	3.72	2.63	2.78	2.42	4.06	5.37	5.26	2.27	2.24	9.5	4.6	12.6	11.1	9.5	7.9	5.7	5.0	7.5	5.5	6.1	8.7	12.5	8.1	13.9
Dy	17.4	19.4	14.5	14.5	12.9	21.8	32.8	32.1	12.6	12.3	55.5	24.5	67.3	59.4	59.4	42.9	26.8	19.4	30.3	24.0	27.1	41.3	63.1	38.9	78.2
Ho	2.90	3.36	2.59	2.59	2.37	3.92	6.09	5.97	2.36	2.32	10.1	4.5	12.7	11.3	12.0	8.8	4.9	3.6	5.5	4.5	4.9	7.9	10.9	7.1	15.1
Er	7.14	8.71	7.11	6.78	6.51	10.2	15.3	15.1	6.66	6.50	26.7	12.5	37.9	33.6	36.3	26.8	14.2	11.3	16.1	13.5	14.3	22.7	27.5	19.5	44.3
Tm	0.855	1.11	0.988	0.911	0.881	1.28	1.83	1.79	0.927	0.883	3.3	1.7	5.4	4.8	5.1	3.8	2.0	1.6	2.3	1.9	2.0	3.0	3.4	2.6	6.3
Yb	5.34	7.17	7.00	6.07	5.87	8.03	11.1	10.9	6.41	5.93	20.7	11.5	35.9	32.0	32.7	25.3	13.4	11.7	15.7	13.3	13.9	19.8	20.9	17.6	42.9
Lu	0.732	1.01	1.04	0.933	0.873	1.12	1.54	1.52	0.930	0.847	2.8	1.7	5.1	4.5	4.4	3.6	2.0	1.8	2.3	2.0	2.2	2.8	2.8	2.5	5.9
Hf	1.70	5.20	1.39	1.24	0.845	0.763	1.30	1.29	0.515	0.881	4.8	1.4	3.9	4.8	3.9	2.7	3.6	2.5	3.2	3.6	2.4	4.4	4.2	3.7	7.2
Ta	11.9	32.3	1.95	91.0	30.3	6.70	2.06	2.07	5.26	<dl	29.6	74.5	<dl	5.2	0.7	4.0	<dl	2.8	<dl	<dl	2.1	<dl	0.3	2.6	7.6
Th	117.6	219.7	66.7	35.1	34.3	66.1	192.6	190.2	53.1	25.2	284.5	136.1	773.1	781.1	376.7	919.8	986.8	404.7	452.2	626.9	366.5	494.0	578.4	751.8	928.5
U	20.6	5.76	2.04	70.1	41.2	73.4	15.9	15.4	32.4	7.20	45.3	20.4	14.2	12.9	22.0	11.7	6.4	6.0	11.9	13.6	13.1	15.6	9.4	6.2	21.8
La/Yb	59	41	19	47	20	44	10	12	17	25	21	25	14	14	3	58	99	202	213	163	169	186	178	126	63

<dl: below detection limit for the method (Three times the standard deviation of the total procedural blank).

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measurements of multiple single-element (La, Ce, Pr, Nd) standard solutions spanning the full range of expected concentrations. The trace-element concentrations for the samples from the Bjørndalen transect are presented in Table 1.

Mineralogy and petrology of the samples

Based on the degree of rødbergitic alteration, the samples were divided into three major rock types: carbonatite, transitional rødbergite and rødbergite. General signs of rødbergitization were a change in colour from whitish carbonatite to reddish rødbergite, grain-size reduction and the occurrence of veins.

Carbonatite

The rock type 'carbonatite' represents the unaltered and weakly altered calcite-dolomite carbonatite with a grey to whitish colour and a grain size of ~2 mm. The calcite-dolomite carbonatite consists of primary calcite, dolomite, apatite, pyrite, magnetite and columbite with accessory quartz, baryte, pyrochlore, fluorite and REE fluorocarbonates (e.g. synchysite-(Ce) and parisite-(Ce); Fig. 2a–c). Apatite occurs as hypidiomorphic lozenge-shaped crystals, or aggregates with a preferred orientation producing slightly bluish layers (Fig. 2a,b). The carbonate minerals have a uniform, ~2 mm grain size in hand specimen but reveal in the BSE image a fine irregular intergrowth of calcite and dolomite. Pyrite is present as euhedral cubes (0.5 mm) or larger xenomorphic aggregates together with fluorite and REE fluorocarbonates (Fig. 2c), where columbite forms equidimensional crystals (~0.5 mm). REE fluorocarbonates are the main mineral host for REE in carbonatite and can be found as small (5–20 µm) idiomorphic to hypidiomorphic crystals distributed homogeneously as inclusions in calcite, dolomite and apatite, as well as in the form of larger grains (20–50 µm) in pyrite-fluorite aggregates (Fig. 2c). The small crystals of REE fluorocarbonates can contain Th (up to 8 wt.%). Some carbonatite samples show no evidence of alteration whereas other samples show incipient features of alteration such as the change from the primary whitish grey colouration to beige and earthy colours. The change in colour is caused by Fe oxides which preferentially invade along fractures and grain boundaries. The matrix in the vicinity of these Fe-oxide veins is dominated by a halo of fine-grained calcite. The carbonate minerals in the matrix display a speckled appearance in the BSE image caused by fine disseminated

Fe oxides (<5 µm). The breakdown of pyrite is also a sign of incipient alteration with hematite replacing pyrite aggregates along grain boundaries forming a mosaic texture. In areas of alteration, REE fluorocarbonates are found exclusively enclosed by pyrite and the boundaries of the REE fluorocarbonates are irregular and crosscutting, indicating replacements by hematite (Fig. 2d).

Transitional rødbergite

Transitional rødbergite is a massive calcite-dolomite carbonatite with clear signs of alteration to rødbergite. Transitional rødbergite shows a mix of beige, yellow and greyish coloured irregularly shaped patches where calcite and dolomite are again the principal minerals with accessory baryte, quartz, Ba-bearing phlogopite, apatite, pyrite and monazite-(Ce) (Table 2). Calcite and dolomite have a grain size of <200 µm and show a fine, irregular intergrowth. Baryte is distributed evenly in the samples and forms xenomorphic crystals (50 µm to 1 mm). Ba-bearing phlogopite, however, is concentrated in veins and in the matrix between veins. Transitional rødbergite from the eastern part of the Bjørndalen transect has a high vein density of up to two veins per cm² (Fig. 3) compared to the unveined transitional rødbergite from the western Bjørndalen transect. REE fluorocarbonates occur as small homogeneously distributed patches in the matrix of transitional rødbergite, but a large proportion of the REE is hosted in distinct micro-veins described below.

Veins in transitional rødbergite

Three different micro-vein sets can be distinguished in the eastern transitional rødbergite (Fig. 3). They are numbered on the basis of the observed crosscutting relations in the studied transect.

Hematite veins (Vein Set I) are thin (10 µm) straight veins of hematite and clay minerals.

Monazite veins (Vein Set II) consist of Ba-bearing phlogopite, baryte ± monazite-(Ce), chlorite and hematite. Monazite-(Ce) (100 µm × 30 µm) is enclosed by Ba-bearing phlogopite and found in intergrowth with hematite. In the vicinity of vein set II are irregular patches of monazite-(Ce) within the matrix. Set II veins are the most common veins and are parallel to each other but occasionally branch and display an irregular shape. Pyrite is found as idiomorphic cubes in the vicinity of or in contact with set II veins. Veins partially of monazite engulf older patches of quartz-baryte aggregates.

Allanite veins (Vein Set III) consist of calcite with minor amounts of baryte, dolomite, coarse-grained allanite (0.3 mm × 2 mm) and rarely coarse-grained

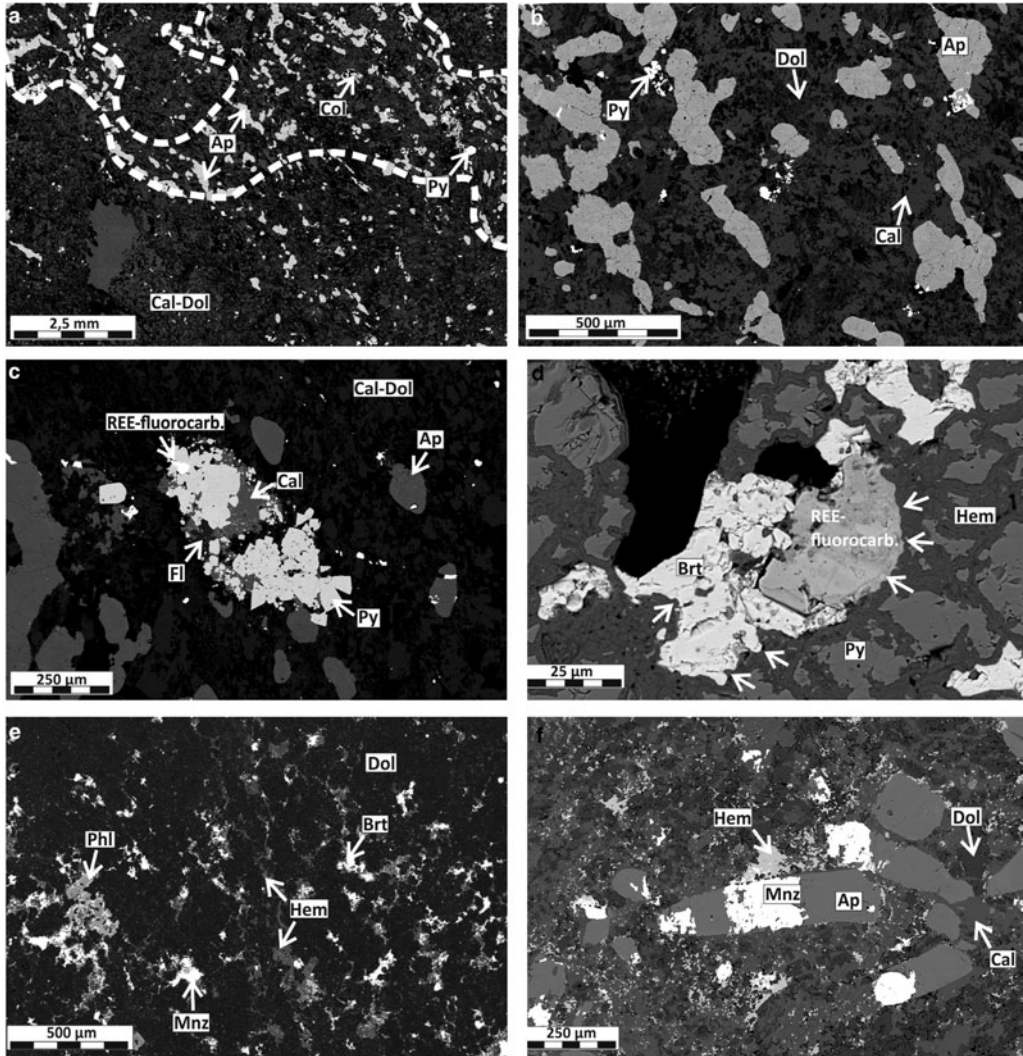


FIG. 2. BSE-SEM images showing the mineralogical and textural changes as a result of rødbergitization in samples from the Bjørndalen transect of the Fen Complex. (a) Apatite-rich carbonatite domains in carbonatite in sample 15-82-FE. (b) Close-up of the texture of a primary carbonatite (sample 15-82-FE) with apatite showing a preferred orientation. The matrix is comprised of an intergrowth of calcite (brighter grey) and dolomite (darker grey). (c) REE fluorocarbonates associated with fluorite and pyrite in primary carbonatite (sample 15-82-FE). (d) Primary pyrite replaced by veins of secondary hematite. REE fluorocarbonates and baryte inclusions at the centre of the altered pyrite are partly replaced by hematite (white arrows). Altered part of sample 15-82-FE. (e) Texture of rødbergite matrix showing fine-grained dolomite with a fine dense network of hematite, baryte and monazite-(Ce) replacing dolomite along grain boundaries (sample 15-89-FE). (f) Texture of a rødbergite matrix similar to (d) showing dolomite-calcite matrix with a fine dense network of hematite along grain boundaries. Monazite-(Ce) is partly replacing apatite (sample 15-88-FE). Mineral abbreviations used: Ap – apatite, Cal – calcite, Phl – phlogopite, Brt – baryte, Col – columbite, Dol – dolomite, Fl – fluorite, Hem – hematite, Py – pyrite, Mnz – monazite-(Ce).

TABLE 2. Summary of the essential and accessory minerals observed in carbonatite, transitional rødbergite, and rødbergite along the Bjørndalen transect.

Carbonite	Transitional rødbergite	Rødbergite
Main minerals		
Calcite	Calcite	Dolomite
Dolomite	Dolomite	Fe dolomite
Apatite		Baryte
Pyrite		Hematite
Columbite		Ba-bearing biotite
Accessory minerals		
Quartz	Baryte	Calcite
Baryte	Ba-bearing biotite	Apatite
Pyrochlore	Apatite	Quartz
Fluorite	Monazite-(Ce)	Monazite-(Ce)
REE fluoro-carbonate	Quartz	
	Hematite	

synchisite-(Ce). The allanite veins are significantly thicker (300 μm) than both set I and II veins.

Rødbergite

The rock type 'rødbergite' is intensely altered massive carbonatite with a fine crystalline carbonate matrix coloured in different shades of red. Porosities, determined from large-area scanning electron microscopy image mosaics, are <2%. Rødbergites consist of varying proportions of dolomite, Fe-dolomite, baryte, Ba-bearing phlogopite, hematite with accessory apatite, calcite, monazite-(Ce), quartz and Ba-bearing feldspar. The matrix consists of idiomorphic to xenomorphic dolomite surrounded by a network of calcite grains with small hematite inclusions (Fig. 2e). While some parts of the matrix display a fine intergrowth of calcite and dolomite, other parts display a coarser crystal size and show evidence for the replacement of dolomite by calcite. Hematite can be found in veins, along crystal boundaries and as inclusions in carbonate minerals. Rødbergite also contains set II monazite veins that

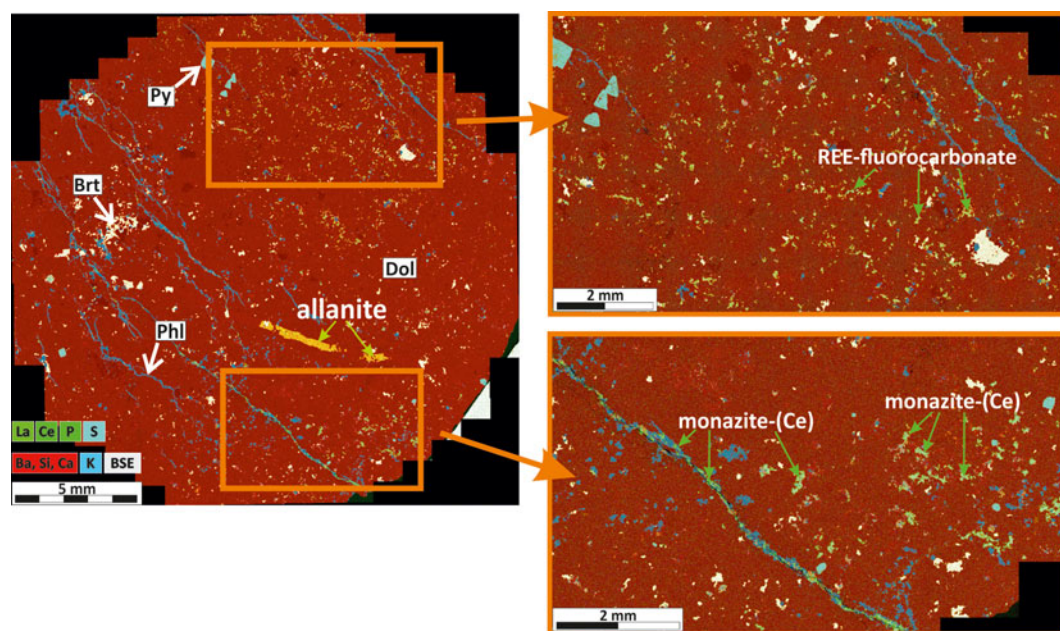


FIG. 3. Large-area chemical map of a transitional rødbergite (sample 15-93-FE) with clearly recognizable micro-veins. REE fluorocarbonates (yellowish) are randomly distributed in the upper part of the polished block. Monazite-(Ce) (green) can be observed in vein set II and in the matrix proximal to vein set II. Allanite (yellow) is part of vein set III. Image obtained by merging >200 EDS maps acquired on an SEM.

show an undulating to *en echelon* pattern. Irregularly shaped baryte-phlogopite patches (0.2–2 mm) contain clusters of idiomorphic to hypidiomorphic blade-shaped phlogopite (100 μm). Baryte is generally associated with phlogopite but can incorporate relicts of a hematized dolomite-calcite matrix or have a hematite rim. Both phlogopite and baryte are unaltered and show little or no inclusion of hematite. The energy-dispersive X-ray spectroscopy back-scattered electron (EDS-BSE) elemental maps reveal a mild halo of higher Ca concentrations in matrix carbonates in the vicinity of baryte-phlogopite veins (set II).

Apatite-rich inclusions (relicts)

Some r dbergite samples display prominent rounded elliptical inclusions ($\varnothing \sim 5\text{--}10 \text{ mm}$) surrounded by the fine, red irregular carbonate matrix of r dbergite. These inclusions are dominated by apatite and dolomite with minor amounts of baryte, hematite, phlogopite and monazite-(Ce) (Fig. 4). Apatite is an early liquidus phase in carbonatite magma, and apatite-rich layers, frequently disrupted by magmatic and post-magmatic processes, are common in carbonatites and are generally interpreted as cumulates (Hornig-Kjarsgaard, 1998; Ihlen *et al.*, 2014; Chakhmouradian *et al.*, 2017). Andersen (1987a) and Schilling (2013) also described apatite cumulate inclusions in calcite carbonatite of the Fen Complex. Our observations show that similar apatite inclusions were present in the carbonatite in Bj rdalen and survived the later r dbergitization event as apatite-rich relicts. The central part of the apatite relicts consist of a primary polycrystalline apatite aggregate with dendritic patches of dolomite, baryte and phlogopite. The apatite relicts are partly replaced and the amounts of secondary baryte, phlogopite and dolomite increase towards the rim. The rim itself is completely replaced by secondary minerals and displays a strong concentration of secondary monazite-(Ce) with up to $\sim 20\%$ of the outer 500 μm layer. The formation of monazite at the expense of apatite is a common process caused by the interaction of carbonatite with hydrothermal fluids (Chakhmouradian and Mitchell, 1998; Moore *et al.*, 2015; Giebel *et al.*, 2017). Monazite-(Ce) is often found as an intergrowth with baryte or as polycrystalline elongated aggregates with sizes up to 1 mm. In the vicinity of monazite-(Ce) a higher concentration of calcite is detectable in the carbonate matrix. Monazite-(Ce) is the major REE mineral in the r dbergite and is mainly distributed around the apatite relicts and intergrown with baryte in monazite veins (set II) and the r dbergite matrix.

Primary and secondary mineral assemblage

There is clear textural evidence that the primary minerals of the igneous carbonatite are systematically replaced by a secondary mineral assemblage (Table 2), and this mineralogical change is associated with a systematic variation of REE concentrations in the geochemical profile along the Bj rdalen transect (Fig. 5). Carbonatites of the Bj rdalen transect consist mainly of coarse primary calcite, dolomite, apatite, magnetite, pyrite and columbite. The dominant REE carriers in these carbonatites are REE fluorocarbonates (e.g. synchysite-(Ce)/bastn site-(Ce)). Initial alteration of primary carbonatite can be recognized by the development of a fine network of hematite veins along carbonate grain boundaries. As the proportion of fine disseminated hematite between grain boundaries increases, it produces a stronger red colouration in the rock, hence the name r dbergite. The alteration therefore consists of oxidation (of magnetite and pyrite to hematite), recrystallization and replacement of primary minerals, leading to a secondary mineral assemblage of Fe-dolomite, baryte, phlogopite and hematite and accessory calcite, monazite-(Ce), quartz and Ba-bearing feldspar.

REE fluorocarbonates are partially or completely replaced during alteration. The main REE carrier in r dbergite is monazite-(Ce) and minor allanite. Allanite is found exclusively as part of allanite vein set III in transitional r dbergite. Monazite-(Ce) can be found in monazite vein set II and in the matrix close to monazite veins. The zone of transitional r dbergite with the highest concentration of REE also has the highest density of veining. The fully transformed r dbergite has a much lower density of veins and there is an analogy with replacement skarn deposits where the margins of replacements are characterized by vein skarn (feeder fractures), whereas massive skarn shows no clear vein assemblage (Kim *et al.*, 2015). Monazite-(Ce) in r dbergite is mainly distributed around the rims of apatite-rich relicts and to a lesser extent in monazite veins.

The main host minerals for Th are monazite-(Ce), thorite and REE fluorocarbonates. The Th concentration in monazite-(Ce) found in the monazite veins in the transitional r dbergite is mainly below the detection limit of the EDS SEM ($<0.5 \text{ wt.}\%$).

Geochemical results

The Bj rdalen transect in the Fen complex provides a complete record of the gradual transformation from igneous carbonatite to r dbergite (Fig. 5). The

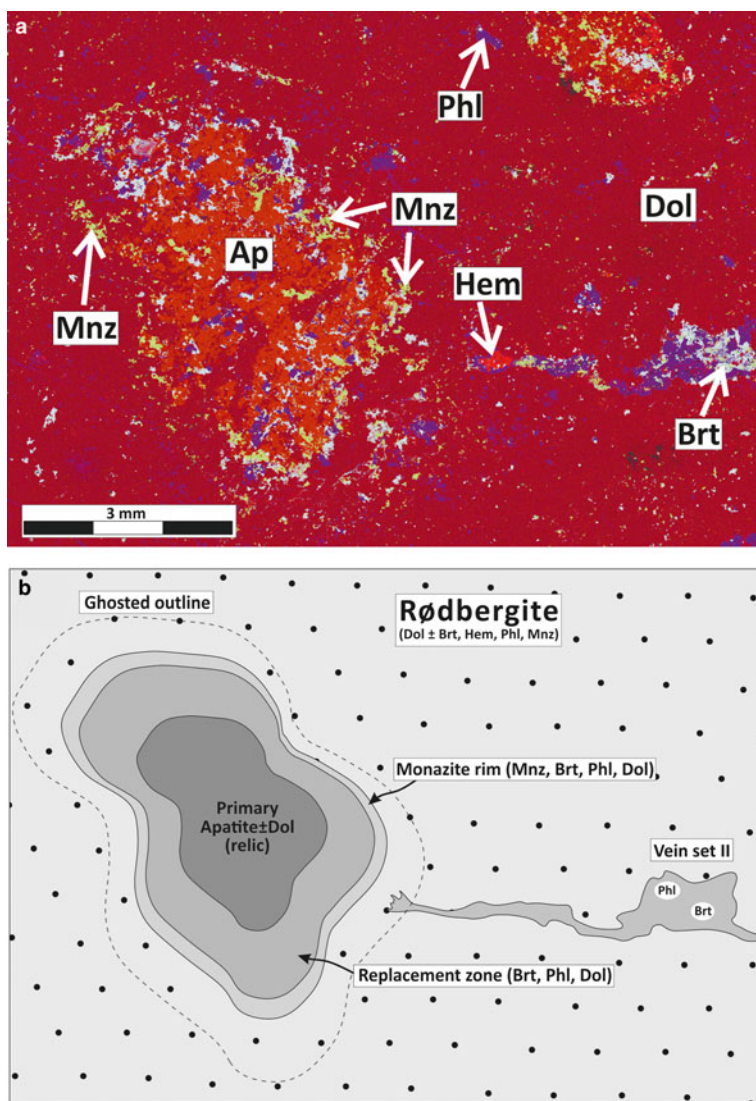


FIG. 4. Large-area chemical map (a) and line drawing (b) of an 'apatite trap' for REE mineralization in rødbergite (sample 15-90-FE). (a) Large area chemical EDS-SEM map of a rødbergite illustrates the distribution of monazite-(Ce) (green-yellow) on the outer rim of a relic of a primary apatite-inclusion-bearing carbonatite, partly replaced during rødbergitization. A rootless baryte-phlogopite vein (set II) – a possible feeder fracture – can be seen to the right of the apatite relic. Mineral abbreviations: Ap – apatite, Phi – phlogopite, Brt – baryte, Hem – hematite, Mnz – monazite-(Ce). (b) Schematic diagram showing the replacement of the apatite relic. Transport of the replacement fluid occurred along set II veins, which are comprised of baryte, phlogopite ± hematite and monazite-(Ce). The ghost outline can be seen by the concentration of replacement minerals, e.g. monazite-(Ce). The outer rim of the apatite relic is significantly enriched in monazite-(Ce) plus baryte, phlogopite and dolomite. The replacement zone is a mix of primary apatite and secondary minerals like baryte and phlogopite. The core of the apatite relic consists mainly of primary apatite and dolomite.

progressive alteration is clearly visible at outcrop scale due to a change in colour (reddening) and texture (grain size reduction) of the rock. This change

in colour and texture is associated with a systematic change in mineral composition and elemental concentration of the altered carbonatite (Table 2).

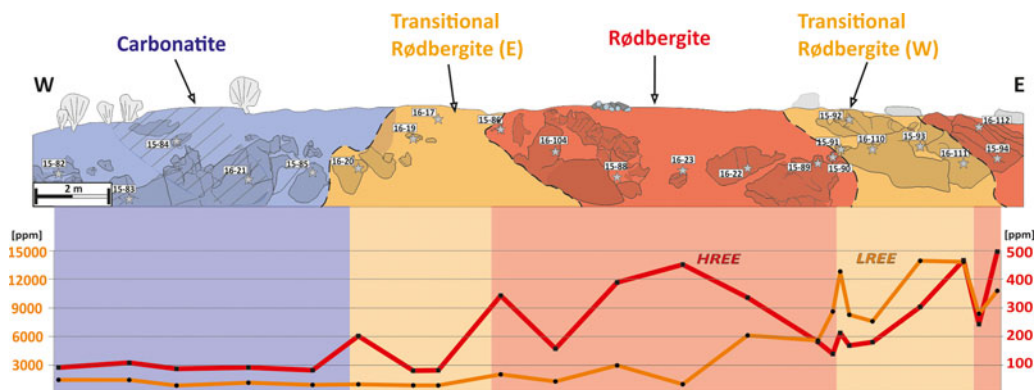


FIG. 5. Sketch of the Bjørndalen transect, which is divided into three different alteration zones. Rødbergite (strong alteration) is found in the centre and western end of the transect and is marked by a red coloration. Transitional rødbergite (mild alteration) is shown in orange and surrounds the central rødbergite. Primary or very weakly altered carbonatite at the western end is marked in blue. The most primary-looking samples were taken from the hatched area. Rocks that outcrop are shaded slightly. The primary carbonatite and the eastern transitional rødbergite are showing low concentrations of *HREE* and *LREE*. High values for *HREE* are in the rødbergite area, and *LREE* is heavily enriched in the western transitional rødbergite.

The primary igneous carbonatites have the lowest concentrations of *REE* (≤ 1600 ppm *TREE*) and Th (≤ 220 ppm) within the Bjørndalen transect (Fig. 5). Samples from the transitional rødbergites show a relatively large variation in *REE* concentrations. The western transitional rødbergites are only slightly enriched in *REE* compared to unaltered carbonatite, whereas the eastern transitional rødbergites contain the highest concentration of *REE* for the whole Bjørndalen transect ($\leq 16,000$ ppm *TREE*). Although the western and eastern transitional rødbergites appear to be very similar, the eastern transitional rødbergites shows a high density of micro-veins (set I–III). Fully transformed rødbergite is significantly enriched in *REE* (1200–11,000 *TREE*) and has the highest concentration of Th within the transect (≤ 1000 ppm). All of the samples are *LREE*-dominated and show high La/Yb ratios relative to chondritic ratios (Fig. 6). The ratio of La/Yb differs throughout the transect and is generally higher in the eastern transitional rødbergite (Fig. 6d), compared to the rødbergite (Fig. 6c) and the western transitional rødbergite (Fig. 6b). High values of La/Yb correspond to the overall amount of monazite-(Ce). Monazite separates *LREE* and *HREE* much more efficiently than apatite or calcite and therefore causes higher La/Yb ratios (Chakhmouradian *et al.*, 2016). The highest *HREE* concentrations are found in rødbergites (up to 650 ppm total *HREE*) with La/Yb ratios extending to very low values (< 20 , but as

low as 3 for sample 16–23). The elemental distribution in the Bjørndalen transect produces a zonation with Th and *HREE* concentrated in rødbergite at the centre of alteration zone, and *LREE* locally concentrated in transitional rødbergite with a high vein density.

Discussion

The progressive alteration from carbonatite to rødbergite along the Bjørndalen transect is associated with a significant enrichment of *REE* in the altered samples relative to the primary igneous carbonatite. Mineralogical analysis for the present study has shown that the main cause of this enrichment is the precipitation of secondary monazite-(Ce) and the occurrence of monazite and allanite veins, all associated with the rødbergite-forming process.

Primary carbonatite

Carbonatites are significantly more susceptible to changes in their primary magmatic texture than silicate rocks and their evolution commonly involves a variety of post-magmatic processes, including exsolution and subsolidus re-equilibration with carbothermal-derived fluids (Chakhmouradian *et al.*, 2015; Broom-Fendley *et al.*, 2016). Because the focus of this paper is the rødbergitization, the

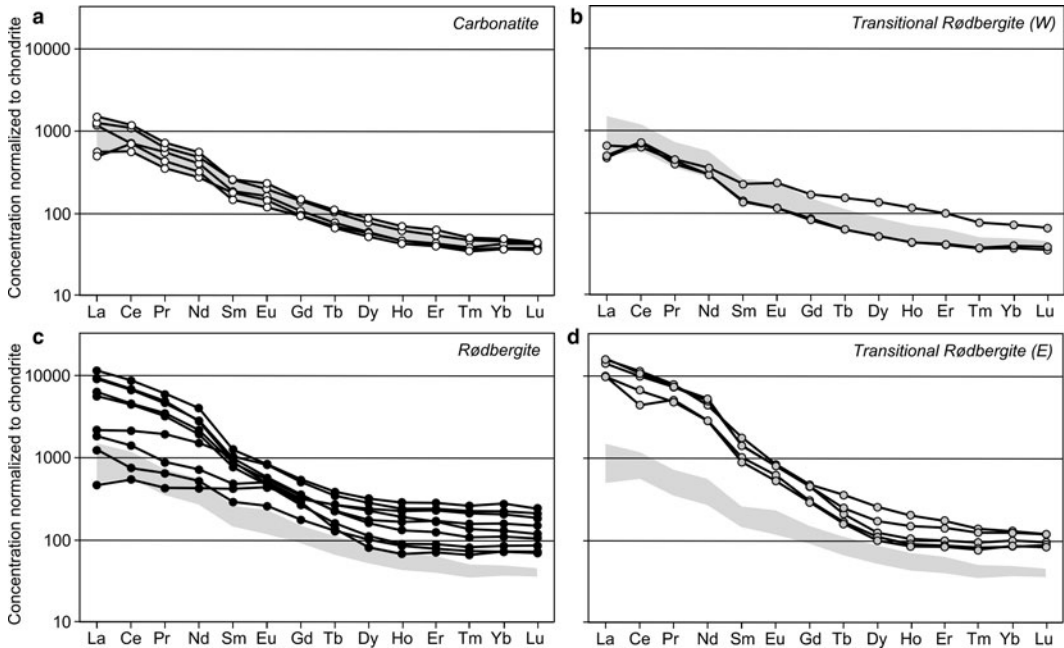


FIG. 6. REE concentrations determined by ICP-MS for Bjørndalen samples normalized to CI1-chondrite values from McDonough and Sun (1995). (a) Igneous carbonatites show a relative enrichment of LREE to HREE with a moderately decreasing slope towards HREE. (b) The western zone of transitional rødbergite has a similar REE distribution to the primary igneous carbonatites, with one sample showing HREE enrichment; (c) The eastern veined transitional rødbergites are distinctly different with high concentrations of LREE and a steep, slightly irregular slope of the REE graph. (d) Rødbergite samples show a range of REE patterns with some samples having a flat HREE slope and relatively high HREE concentrations not accompanied by large LREE enrichments compared to primary carbonatites. Other rødbergite samples show a strong LREE enrichment similar to the eastern veined transitional rødbergites, but with generally higher concentrations of HREE. The field defined by REE concentrations in primary carbonatites is shown in light grey.

term ‘primary carbonatite’ used here includes rocks affected by early post-magmatic processes prior to the rødbergitization. The fine-grained intergrowth of calcite and dolomite in the matrix of primary carbonatite samples from the Bjørndalen transect is almost certainly, in part, the product of post-magmatic dolomitization. According to Chakhmouradian *et al.* (2016) dolomite has a much smaller capacity to build in REE than calcite (up to 2000 ppm REE). During the dolomitization, the excess REE will be released, which could have been an initial REE source forming the accessory REE fluorocarbonates in the primary carbonatite.

As argued by Andersen (1989) and this study, the hydrothermal event causing the formation of rødbergite involves an intense reaction of carbonatite with an oxidizing, at least partly external fluid. The formation of rødbergite discussed here therefore goes well beyond the classical early

post-magmatic processes of exsolution and subsolidus re-equilibration in carbonatites. The formation of the major minerals e.g. calcite, dolomite, apatite and pyrite happened before the rødbergitization. On the other hand, there is textural evidence that the accessory minerals in the primary carbonatite listed in Table 2 are in part secondary in nature. Based on the available evidence this could be the result of post-magmatic processes or the remote alteration halo of the rødbergitization.

Secondary nature of monazite-(Ce)

Monazite-(Ce), the dominant REE mineral in rødbergite and transitional rødbergite, is paragenetically related to the secondary assemblage of hematite, baryte and phlogopite, and closely spatially associated with primary apatite-dolomite relics. The concentration of secondary monazite-(Ce) in the

outer rim of primary apatite-dolomite relics in r dbergite and transitional r dbergite can be explained as a replacement reaction. While the alteration fluid was penetrating the carbonatite through grain boundaries and veins, hematite, baryte, phlogopite and carbonates were precipitated together with minor monazite-(Ce). When the hydrothermal fluid interacted with apatite, *REE* preferentially precipitated the *REE* phosphate monazite-(Ce), by either partial or full replacement of apatite. This observation can also be made for smaller apatite crystals, which are completely pseudomorphed by monazite-(Ce) (Fig. 2f). Hence apatite, in particular the apatite-rich relics, acted as a *REE* ‘trap’ during the formation of r dbergite.

REE stability in hydrothermal fluids in the Fen Complex

The evidence for breakdown of *REE* fluorocarbonates in igneous carbonatites and the strong enrichment of *REE* in r dbergites – by formation of secondary *REE* minerals in the matrix, in veins and around apatite ‘traps’ – are evidence for solubility and mobility of *REE* in the fluids that caused the ‘r dbergitization’. Several experimental studies have emphasized the important role of fluoride, sulfate and chloride ligands to form stable *REE* complexes in hydrothermal fluids at 200–400°C in geological environments (Williams-Jones *et al.*, 2012; Williams-Jones and Migdisov, 2014), with *REE* sulfate complexes dominating at temperatures >300°C in weakly acidic fluids (Migdisov and Williams-Jones, 2014). The ubiquitous presence of baryte as part of the secondary assemblage in r dbergite, including in the monazite and allanite veins, suggests an important role for sulfate complexes in the Fen Complex. In addition, experimental studies have shown that sulfate inhibits the formation of monazite from fluorapatite (Harlov and F rster, 2004), which highlights the importance of baryte precipitation coupled with monazite-(Ce) formation (Feng *et al.*, 2016). Sulfate was probably formed by breakdown of primary sulfides in carbonatites when they reacted with an oxidizing hydrothermal fluid.

Experimental studies have further demonstrated that the stabilities of *REE* fluoride, -sulfate and -chloride complexes decrease strongly with decreasing temperature and increasing pH (Williams-Jones *et al.*, 2012; Migdisov and Williams-Jones, 2014; Williams-Jones and Migdisov, 2014). Therefore, cooling of the hydrothermal fluid, or reaction with

carbonate host rocks leading to a pH-increase in the fluid, are in general suitable geological mechanisms triggering precipitation of *REE* minerals from aqueous solutions. Of particular relevance to the Fen Complex is the experimental evidence that fluid–rock reactions of fluorine- and sulfate-bearing aqueous fluids with phosphate-rich host rock is a highly effective trigger for the destabilization of the aqueous *REE* complexes, resulting in the precipitation of *REE* phosphate minerals such as monazite-(Ce) (Migdisov and Williams-Jones, 2014; Louvel *et al.*, 2015). This mechanism fully explains the textural evidence that relics of cumulate apatite layers acted as a trap for *REE* via the crystallization of monazite-(Ce) in r dbergite in the Fen Complex.

Evidence for lanthanide tetrad effects?

The chondrite-normalized *REE* patterns differ from smooth continuous curves and display steps and rounded segments for blocks of *REE* (Fig. 6; see also supplementary Fig. S1, details below). These patterns cannot simply be explained by the different ionic radii of the *REE* and are generally referred to as the ‘tetrad-effect’ of the lanthanides, where the chondrite-normalized distributions are split into four concave or convex segments (La-Nd, (Pm)-Gd, Gd-Ho and Er-Lu) called tetrads (Monecke *et al.*, 2002). The origin of the lanthanide tetrad effect is the subject of ongoing discussions, and the effect is not commonly observed in geological materials, with the exception of evolved granites with a high-temperature hydrothermal component (Irber, 1999; Monecke *et al.*, 2002). Recent results suggest that the tetrad effect in highly evolved granites can be caused by the fractionation of monazite and xenotime (Duc-Tin and Keppler, 2015). Our initial results suggest that there are concave patterns for the first tetrad (La-Ce-Pr-Nd) in carbonatites and r dbergites, and convex patterns for the 2nd ((Pm)-Sm-Eu-Gd) and 3rd tetrad (Gd-Tb-Dy-Ho) in transitional and fully altered r dbergites (supplementary Fig. S1), but this is the subject of ongoing work.

LREE and HREE decoupling

The geochemical results assembled here also show clear evidence for a decoupling of *LREE* and *HREE* during the formation of r dbergite, and monazite-(Ce) and allanite veins interpreted as feeder fractures very highly enriched in *LREE*. Experimental work has shown that at temperatures

of $>150^{\circ}\text{C}$ aqueous *LREE* complexes are generally more stable than *HREE* complexes, in particular those involving fluoride as the ligand (Williams-Jones *et al.*, 2012). In geological terms, this means that *HREE* drop out of solution first when aqueous *REE* complexes are destabilized, and that *LREE* remain in solution longer and are transported over longer distances compared to *HREE*. For instance, Williams-Jones *et al.* (2012) showed how a temperature drop of a *REE*-bearing fluid in a feeder vein system resulted in a distinct fractionation of *REE*, with the *LREE* being transported further along the feeder veins, down the temperature gradient.

Therefore, the observed *LREE*-*HREE* decoupling and the concentration of *HREE* in the central rødbergite in the Fen Complex can be explained by their relative immobility compared to *LREE*. *HREE* are precipitated in the area of strongest alteration (rødbergite), whereas *LREE* remained in solution and were transported further away from the centre of alteration domain, into the alteration halo (now represented by the transitional rødbergites). The hydrothermal monazite and allanite micro-veins are an inherent part of the rødbergite formation process, and where these veins (possible feeder fractures) are abundant, as in the eastern transitional rødbergite zone, there is the strongest enrichment of *LREE* in the bulk-rock samples.

Th enrichment during rødbergitization

Thorium is enriched in rødbergite along the Bjørndalen transect in a similar pattern to *REE*. *HREE* and Th are most enriched in rødbergite (relative to transitional rødbergite and carbonatite (Table 1). Secondary Th minerals (thorite) and secondary Th-bearing minerals such as monazite-(Ce) are associated with the rødbergitization. Samples that show a significant *LREE* concentration due to a high density of *REE* mineral bearing veins do not show elevated Th concentrations. Therefore Th was probably less mobile than *LREE* and precipitated earlier, together with the *HREE*, in the centre of the alteration domain.

Nature of the hydrothermal fluids in the Fen Complex

A comparison between the primary and secondary assemblages described here suggests that the hydrothermal fluids involved in the formation of rødbergite and in the observed *REE* enrichment were more oxidized than the primary magnetite-

pyrite-bearing carbonatites; this oxidized character must have been acquired outside of the Fen Complex. Furthermore, Andersen (1984) presented strontium and oxygen isotopic evidence to show that fluids involved in rødbergite formation had high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and elevated $\delta^{18}\text{O}$. This suggests that the fluids involved in the *REE* mineralization in the Fen Complex were not simply evolved melt-like hydrous fluids; such late-magmatic fluids often play a critical role in producing high grades in *REE* resources (Wall and Mariano, 1996; Duraiswami and Shaikh, 2014; Smith *et al.*, 2016; Bodeving *et al.*, 2017). Instead, the rødbergite fluids were hydrothermal and had at least partly equilibrated with Precambrian quartzofeldspathic gneisses outside of the Fen Complex, and possibly with groundwater (Andersen, 1984). It has been well documented that *REE* can be highly mobile in such fluids, producing *REE* mineralization well outside of their magmatic source rock. This has been shown for carbonatites, e.g. Kangankunde (Wall and Mariano, 1996), as well as for peralkaline complexes, e.g. Strange Lake (Gysi and Williams-Jones, 2013). Sediment-hosted replacement-type carbonatite *REE* deposits, e.g. Bayan Obo (Campbell and Henderson, 1997; Wu, 2008; Smith *et al.*, 2015), breccia-hosted Fe-Cu-Au-*REE* deposits, e.g. Olympic Dam (Oreskes and Einaudi, 1990; Groves and Vielreicher, 2001; McPhie *et al.*, 2011), and unconformity-type *REE*±U deposits, e.g. Athabasca Basin (Fayek and Kyser, 1997) are examples of even more distal deposits for which a link with fluids sourced by igneous carbonatite at depth have been proposed. The *REE* mineralization of Mount Weld, in particular, shows similar processes with an horizon of secondary monazite within carbonatite laterite produced by groundwater alteration of apatite (Lottermoser, 1990; Smith *et al.*, 2016).

A model for rødbergite formation

The present findings are not fully consistent with the existing model of Andersen (1984, 1986) for the *REE* mineralization in rødbergite of the Fen Complex. A key element of the existing model involves a progressive residual enrichment of insoluble *REE* minerals by leaching and removal of the carbonate minerals during hydrothermal alteration (Andersen, 1984). Both Andersen's model and our model proposed here involve post-magmatic oxidizing hydrothermal fluids which equilibrated with rocks outside of the Fen

Complex. The present authors believe, however, that the *REE* concentration cannot be explained solely by a residual enrichment of primary *REE* minerals for the following reasons: (1) The main *REE* carrier mineral changes from *REE* fluorocarbonate in the carbonatite, to monazite-(Ce) in the r dbergite, and this change must have involved the dissolution and reprecipitation of *REE*. Textural evidence has been presented here for the progressive breakdown and dissolution (leaching) of primary *REE* fluorocarbonates from the primary igneous carbonatites by a hydrothermal fluid. (2) The monazite-(Ce) in the r dbergite is predominantly found in a network of fine veins and is highly enriched where these veins are in contact or closely associated with primary apatite-dolomite relics as a result of the replacement of apatite by monazite-(Ce), with the apatite relics acting as a *REE* trap. These textures require *REE* to be transported in a fluid phase, and they have not been observed in primary carbonatite. (3) *REE* enrichment by more than an order of magnitude from carbonatite to r dbergite is observed in the Bj rmdalen transect. This would require a major volume reduction by 90% and would be predicted to be accompanied by formation of porous rocks with cavernous mineral assemblages (Chakhmouradian *et al.*, 2015), as well as collapse breccias. No field evidence for extensive brecciation (Andersen, 1987a), or formation of highly porous, vug-rich rocks is apparent in the Bj rmdalen transect.

We propose a general model for the formation of r dbergite in the studied transect at Bj rmdalen that is consistent with our findings and that can also be applied to the Fen Complex as a whole. Our model involves leaching of primary *REE* fluorocarbonates from igneous carbonatites by highly oxidizing, fluorine and sulfate-rich fluids, and transport, reprecipitation and concentration of *REE* in monazite-(Ce) in zones of extensive fluid-rock interaction now marked by r dbergitic rocks, surrounded by alteration halos. The progressive alteration of carbonatite to r dbergite in the Bj rmdalen transect by an oxidizing hydrothermal fluid caused the breakdown of primary *REE* fluorocarbonates and precipitation of secondary monazite-(Ce) in r dbergite. This secondary monazite-(Ce) is concentrated along a fine irregular network of veins and around primary apatite-dolomite relics, where monazite-(Ce) is replacing apatite. The secondary monazite-(Ce) together with multiple generations of monazite- and allanite-bearing veins can account for the *REE* enrichment in r dbergite and transitional r dbergite samples by

an order of magnitude more than the primary carbonatite. The relative enrichments of *HREE*, *LREE* and Th are variable throughout the Bj rmdalen transect due to different element mobilities and the density of the *REE* vein networks, which cause the development of overlapping zones of enrichment, with Th and *HREE*-rich zones being closer to the centre of alteration than the *LREE*-rich zone found in the alteration halo.

The above model for *REE* mineralization in the r dbergite has significant implications for a *REE* exploration strategy. The model predicts the existence of separate zones of *HREE*, *LREE* and Th enrichment throughout the Fen Complex. The selective exploitation of *HREE* and *LREE* without high Th concentrations (generally considered an undesirable element in *REE* exploitation) can now be assessed better. Moreover, *LREE* might form an enriched halo further away from the centre of alteration than expected. Because the *REE* mineralization was not formed by passive enrichment of primary *REE* minerals, the alteration fluid must have contained *REE*. Therefore, any rock in the complex (e.g. damtjernite or fenite) that came into contact with the same r dbergite-forming fluid may be a potential exploration target.

Conclusions

The detailed mineralogical and geochemical investigations of the progressive transformation of primary carbonatite to r dbergite has provided new insights into the *REE* concentration processes during the alteration of carbonatite: (1) The progressive alteration is associated with a 10-fold enrichment of *REE* in the altered samples relative to the primary igneous carbonatite. The main cause of this enrichment is the precipitation of secondary monazite-(Ce) in the matrix, and the occurrence of monazite and allanite micro-veins, all associated with the r dbergite-forming process. (2) The breakdown of primary *REE* fluorocarbonates in carbonatites and the formation of monazite-bearing r dbergite is caused by interaction between carbonatite and an oxidizing aqueous hydrothermal fluid, in which *REE* were mobile. (3) We found that secondary monazite-(Ce) is concentrated around apatite-rich relics in r dbergite. These apatite-rich relics acted as a trap for *REE* by triggering the precipitation of secondary monazite-(Ce), a mechanism predicted by physical-chemical experiments. (4) In addition to the enrichment of *REE*, the formation of r dbergite is also associated with an increased concentration of Th. Evidence was

found in the present study, however, for partial decoupling of *LREE*, *HREE* and Th in the Bjørndalen transect, and there are separate zones of *LREE*, *HREE* and Th enrichment.

Building on the model for rødbergite formation by Andersen (1984), the new model for the formation of rødbergite can explain all the reported features and has a significant implication for a future *REE* exploration strategy. The model predicts the existence of separate zones of *LREE*, *HREE* and Th enrichment throughout the Fen Complex and highlights the importance of apatite-rich relics and *REE* mineral veining for high-grade *REE* ore.

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Supplementary material

To view supplementary material for this article, please visit <https://doi.org/10.1180/minmag.2017.081.070>

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